ACCURATE NON-BORN–OPPENHEIMER VARIATIONAL CALCULATIONS OF SMALL MOLECULAR SYSTEMS

by

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A Dissertation Submitted to the Faculty of the
DEPARTMENT OF PHYSICS
In Partial Fulfillment of the Requirements
For the Degree of
DOCTOR OF PHILOSOPHY
In the Graduate College
THE UNIVERSITY OF ARIZONA

2 0 0 6
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Sergiy Bubin
ACKNOWLEDGEMENTS

First of all I must thank my advisor, Ludwik Adamowicz, for guidance, support, healthy criticism, and experience sharing. This concerns not only my research or graduate study in general, but also everyday’s life. Without his help, inspiration and enthusiasm I would probably not even found myself in Tucson that late night on April 23rd, 2001.

I would like to thank several other people: postdoctoral fellows, graduate students, and visitors of the laboratory of theoretical and computational chemistry at Arizona, who contributed (directly or indirectly) to the non-Born–Oppenheimer studies of small molecular systems considered in this dissertation. These people are Donald Kinghorn, Mauricio Cafiero, Eugeniusz Bednarz, Michele Pavanello, Dariusz Kedziera, and Monika Stanke. I am very grateful for very nice environment in the laboratory I enjoyed during my stay there, which was made by everyone working in it.

I should also tender thanks those faculty members at the departments of physics, chemistry, and mathematics whose classes I took to fulfill the official class work requirements. Many of these classes were not only useful but also very enjoyable.

Finally I want to thank my wife Albina for love, emotional support and patience with such a difficult person as myself. She is one of the greatest gifts God gave me in my life.
DEDICATION

I dedicate this work to B.N.
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ABSTRACT

The research overviewed in this dissertation concerns highly accurate variational calculations of small molecular systems without assuming the Born–Oppenheimer approximation. The centerpiece of the research is the use of different forms of explicitly correlated Gaussian basis functions. These basis functions allow analytical evaluation of all necessary matrix elements and provide a very powerful tool for solving quantum mechanical problems encountered in various areas of physics. Most of the derivations presented in the dissertation are done within the formalism of matrix differential calculus that has proven to be a very handy and effective way of dealing with explicitly correlated Gaussians. As this formalism is not widely used in physics or chemistry, some mathematical background is provided. The expressions obtained theoretically were implemented in a computer code that was run quite extensively on several parallel computer systems during the period of the author’s Ph.D. study. The results of many such calculations are presented and discussed. The dissertation is primarily based on the content of the papers that were published in coauthorship with my scientific advisor and other collaborators in several scientific journals. It also includes some topics that were not considered in the publications but are essential for the completeness and good understanding of the presented work.
CHAPTER 1

GENERAL INTRODUCTION

1.1 Introduction

Since the Schrödinger equation, that describes nonrelativistic quantum systems, was introduced in 1926, a large number of works have been devoted to the development of methods that allow to solve the equation numerically for different types of atomic and molecular systems. These efforts have lead to the appearance of such a branch of modern science as quantum chemistry. Over the years, there has been enormous progress in our ability to study molecules to a higher and higher degree of accuracy. However, the requirements for the effectiveness and accuracy of the methods and their numerical implementations have been raising as well. This is caused, primarily, by significant advances in the experimental measurements and by studying new phenomena where very good quantitative description of relatively weak effects plays an important role.

Modern gas phase measurements of molecular quantities such as rovibrational and electronic excitation energies, electron affinities, ionization potentials, bond dissociation, and atomization energies achieve nowadays the precision exceeding tenths or even hundredths of a wave number. This presents a challenge to quantum mechanical calculations because in order to reach such an accuracy not only the electronic component of the wave function has to be calculated with a very high precision, but also the component describing the motion of the nuclei (vibrational and rotational) and the component describing the coupling of the electronic and the nuclear motions has to be very accurately represented. Furthermore, even for small systems the relativistic effects need be taken into account.

In order to keep up with the experiment and address many purely theoretical questions work has to continue on development of more refined theoretical method-
ology, which accounts for nonadiabatic interactions. With such methodology, fundamental concepts of the molecular quantum mechanics can be explored and the basic theoretical framework of the high resolution molecular spectroscopy can be tested. Recent advances in high performance computing, especially in the area of massively parallel systems has given momentum to proceed with the development of quantum mechanical methods that depart from the BO approximation and describe the motions of the nuclei and electrons with a single wave function.

1.2 Significance of the Born–Oppenheimer approximation and its limitations

In an attempt to make the quantum-mechanical calculations on molecular systems practical and to provide a more intuitive interpretation of the computed results, it has long been a quest in the electronic structure theory of molecules to establish a solid base for separating the motion of light electrons from the motion of heavier nuclei. It is believed that the original work of Born and Oppenheimer \[1\] initiated the discussion by the analysis of the diatomic case. Soon after the formalism was extended to polyatomic systems, and by the present time the consideration of the topic has been brought to a level of commonly accepted theory. It would probably not be a mistake to state that the Born–Oppenheimer approximation has been one of the major bases of the quantum chemistry. Most of the quantum chemical calculations done presently are done within the framework of the Born–Oppenheimer (BO) approximation. It allows to simplify the solution of the Schrödinger equation significantly. In this approximation the wavefunction is presented as a product of the electronic and nuclear parts. The electronic part of the wave function is solved for some arrangements of the fixed nuclei and the corresponding total electronic energy is used as a potential energy for the nuclear motion problem. The electronic problem, which takes most of the required computational time, can be in many cases quite accurately and effectively solved using different approaches, depending on the type of the system under consideration and the number of electrons, such as
self consisted field (SCF), Møller-Plesset Many-Body Perturbation Theory (MBPT), Coupled Cluster family of methods (CC), Configuration Interaction (CI), Density Functional Theory (DFT), Quantum Monte Carlo (QMC), etc.

Despite the wide applicability of the BO approximation, there are situations when the correlations in the motion of electrons and nuclei, neglected in the BO approximation play an important role and should be paid proper attention. The effects resulting from the coupling in the motion of electrons and nuclei are more noticeable and physically important in small molecules, especially those containing light atoms like the hydrogen isotopes. In fact, Handy and Lee [2] estimated the importance of diagonal non-BO corrections to such quantities as harmonic frequencies and molecular geometries and found out that those are negligible for most molecules, but more important for molecules containing hydrogen atoms. Even though non-BO effect are quite small in many practical situations, they need be taken into account if one aims for high precision results. Moreover, in some cases, in particular when we deal with the states that are very close to the dissociation, the Born-Oppenheimer approximation may fail completely in describing some properties of the system. The nonadiabatic coupling terms can quickly become large or even infinite (or singular) when two successive adiabatic states become degenerate. Such singular nonadiabatic coupling may not only lead to the breakdown of the Born–Oppenheimer perturbation theory but also may make the application of the perturbation theory inadequate.

In the context of the non-BO calculations, it is particularly interesting to study highly rhovibrationally and electronically excited molecules and clusters, where more significant coupling between the two motions can occur. Essentially, whenever the spacings between electronic excitation levels become comparable to the spacings between the vibrational or rotational levels nonadiabatic effects are likely to be found. Studies of these effect are relevant to astrophysical phenomena, molecule dynamics, and molecular behavior at high temperatures.
CHAPTER 2

MATHEMATICAL FORMALISM

2.1 Hamiltonian and separation of the center of mass

There are several elements in non-BO calculations that distinguish them from the conventional BO calculations. The first one concerns the Hamiltonian. If one neglects the relativistic effects and places the considered system in a laboratory cartesian coordinate frame, the Hamiltonian has a simple form of a sum of one-particle kinetic energy operators for all particles involved in the system plus a sum representing all pair Coulomb interactions between the particles. We will start this chapter from consideration of the Hamiltonian and separating the motion of the center of mass.

Let us assume that we have a system of \( N \) nonrelativistic particles with Coulomb interaction. If \( \mathbf{R}_i, M_i, Q_i \) are the position in the laboratory frame, the mass, and the charge of \( i \)-th particle respectively, then the Hamiltonian of such a system has the following form:

\[
\mathbf{H}_{\text{tot}} = -\sum_{i=1}^{N} \frac{1}{2M_i} \nabla_{\mathbf{R}_i}^2 + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{Q_i Q_j}{R_{ij}},
\]  

(2.1)

where \( \nabla_{\mathbf{R}_i} \) is the gradient with respect to \( \mathbf{R}_i \), and \( R_{ij} = |\mathbf{R}_j - \mathbf{R}_i| \) are interparticle distances. To separate out the translational motion of the center of mass from Hamiltonian (2.1) we place a particle, let us say particle 1, usually with the heaviest mass, at the origin of the internal coordinate system and we refer the other particles to that center particle using the position vectors \( \mathbf{r}_i = \mathbf{R}_{i+1} - \mathbf{R}_1 \). The direct and
inverse coordinate transforms are given by the following expressions:

\[
\begin{align*}
\mathbf{r}_0 &= \frac{M_1}{m_0} \mathbf{R}_1 + \frac{M_2}{m_0} \mathbf{R}_2 + \ldots + \frac{M_N}{m_0} \mathbf{R}_N \\
\mathbf{r}_1 &= -\mathbf{R}_1 + \mathbf{R}_2 \\
\mathbf{r}_2 &= -\mathbf{R}_1 + \mathbf{R}_3 \\
&\quad \vdots \\
\mathbf{r}_n &= -\mathbf{R}_1 + \mathbf{R}_N
\end{align*}
\] (2.2)

\[
\begin{align*}
\mathbf{R}_1 &= \mathbf{r}_0 - \frac{M_2}{m_0} \mathbf{r}_1 - \frac{M_3}{m_0} \mathbf{r}_2 - \ldots - \frac{M_N}{m_0} \mathbf{r}_n \\
\mathbf{R}_2 &= \mathbf{r}_0 + \left( 1 - \frac{M_2}{m_0} \right) \mathbf{r}_1 - \frac{M_3}{m_0} \mathbf{r}_2 - \ldots - \frac{M_N}{m_0} \mathbf{r}_n \\
\mathbf{R}_3 &= \mathbf{r}_0 - \frac{M_2}{m_0} \mathbf{r}_1 + \left( 1 - \frac{M_3}{m_0} \right) \mathbf{r}_2 - \ldots - \frac{M_N}{m_0} \mathbf{r}_n \\
&\quad \vdots \\
\mathbf{R}_N &= \mathbf{r}_0 - \frac{M_2}{m_0} \mathbf{r}_1 - \frac{M_3}{m_0} \mathbf{r}_2 - \ldots + \left( 1 - \frac{M_N}{m_0} \right) \mathbf{r}_n
\end{align*}
\] (2.3)

Here, \( \mathbf{r}_0 \) is the position of the center of mass, and \( m_0 = \sum_{i=1}^{N} M_i \) is the total mass of the system. By using internal coordinates we reduce an \( N \)-particle problem to an \( n \)-pseudoparticle one with \( n \equiv N - 1 \). The resulting internal Hamiltonian is given by,

\[
\hat{H} = -\frac{1}{2} \left( \sum_{i=1}^{n} \frac{1}{m_i} \nabla^2_{\mathbf{r}_i} + \sum_{i \neq j}^{n} \frac{1}{M_1} \nabla'_{\mathbf{r}_i} \nabla_{\mathbf{r}_j} \right) + \sum_{i=1}^{n} q_i q_i \frac{1}{r_i} + \sum_{i<j}^{n} q_i q_j \frac{1}{r_{ij}}
\] (2.4)

where the prime stands for matrix–vector transpose, and \( r_{ij} = |\mathbf{r}_j - \mathbf{r}_i| \). The masses and charges of the pseudoparticles are defined as \( m_i = M_1 M_{i+1} / (M_1 + M_{i+1}) \) and \( q_i = Q_{i+1} \) respectively. For more details on separating the center of mass motion see references [3, 4].

We can combine all pseudoparticle positions and the gradients with respect to these positions in \( n \)-component vectors,

\[
\mathbf{r} = \begin{pmatrix} \mathbf{r}_1 \\ \mathbf{r}_2 \\ \vdots \\ \mathbf{r}_n \end{pmatrix}, \quad \nabla_{\mathbf{r}} = \begin{pmatrix} \nabla_{\mathbf{r}_1} \\ \nabla_{\mathbf{r}_2} \\ \vdots \\ \nabla_{\mathbf{r}_n} \end{pmatrix}
\] (2.5)
The internal Hamiltonian is then conveniently written in the matrix form,

\[ \hat{H} = -\nabla'_r M \nabla_r + \sum_{i=1}^{n} \frac{q_i q_i}{r_i} + \sum_{i<j}^{n} \frac{q_i q_j}{r_{ij}}, \tag{2.6} \]

where \( M \) is an \( n \times n \) matrix with \( \frac{1}{2m_1}, \frac{1}{2m_2}, \ldots, \frac{1}{2m_n} \) on the diagonal and \( \frac{1}{M_1} \) for all off-diagonal elements. Strictly speaking, in place of \( M \) in expression (2.6) we should put \( M \otimes I_3 \), where \( \otimes \) denotes the Kronecker product and \( I_3 \) is a \( 3 \times 3 \) identity matrix. However, for the sake of simplicity, we will skip writing it, as it will be explained in the next section.

2.2 Notations

Before we proceed to consideration of basis functions and evaluation of matrix elements with them, we need to provide certain definitions and introduce appropriate notations. The formalism of matrix differential calculus will be extensively used throughout this work. It has been proven to be a very convenient tool for derivations of matrix elements with different kinds of Gaussian basis functions \([4, 5, 6, 7]\). But, unfortunately, it is rarely applied in physics or chemistry. To avoid possible confusion we will briefly review some basic concepts. For a detailed introduction to this subject we can recommend reference \([8]\).

In our \( n \)-pseudoparticle problem we deal with two kinds of vectors. First are common three-dimensional vectors representing components of different quantities. The other ones are \( n \)-component vectors in particle space, where each component corresponds to a quantity or an operator associated with a certain particle. Since each of those \( n \) components is often a 3-dimensional vector itself, effectively we have \( 3n \) components. In mathematical terms it is a direct product of two spaces. As a result of this fact, we need to use the Kronecker products throughout. For example,
a vector–matrix–vector product may look as follows:

\[ \mathbf{r}'(A \otimes I_3)\mathbf{r} = (x_1, y_1, z_1, x_2, \ldots, z_n) \cdot \begin{pmatrix} A_{11} & 0 & 0 & A_{12} & \cdots & 0 \\ 0 & A_{11} & 0 & 0 & \cdots & 0 \\ 0 & 0 & A_{11} & 0 & \cdots & A_{1n} \\ A_{21} & 0 & 0 & A_{22} & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & A_{n1} & 0 & \cdots & A_{nn} \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ \vdots \\ z_n \end{pmatrix}. \] (2.7)

Here, \( A \) is an \( n \times n \) matrix, and \( A_{ij} \) are its elements. Writing routinely the Kronecker product is quite tedious and at the same time obvious. To simplify the notations we will use the following matrix–vector multiplication convention instead:

\[ \mathbf{r}'A\mathbf{r} = (\mathbf{r}_1', \mathbf{r}_2', \ldots, \mathbf{r}_n') \cdot \begin{pmatrix} A_{11}\mathbf{r}_1 + A_{12}\mathbf{r}_2 + \cdots + A_{1n}\mathbf{r}_n \\ A_{21}\mathbf{r}_1 + A_{22}\mathbf{r}_2 + \cdots + A_{2n}\mathbf{r}_n \\ \vdots \\ A_{n1}\mathbf{r}_1 + A_{n2}\mathbf{r}_2 + \cdots + A_{nn}\mathbf{r}_n \end{pmatrix} 

= A_{11}\mathbf{r}_1'\mathbf{r}_1 + A_{12}\mathbf{r}_1'\mathbf{r}_2 + \cdots + A_{nn}\mathbf{r}_1'\mathbf{r}_n, \] (2.8)

where \( \mathbf{r}_i'\mathbf{r}_j = x_ix_j + y_iy_j + z_i z_j \). Thus, we first carry out all matrix–vector multiplications in \( n \)-dimensional particle space (or in any other space we deal with) treating 3-dimensional vectors \( \mathbf{r}_i \) as numbers and then, at the end, we replace each product \( \mathbf{r}_i'\mathbf{r}_j \) with a dot product. In other words, everywhere a product of two quantities denoting 3-dimensional vectors appears it should be understood as a dot product, unless a special notice is made.

To keep all the derivations clear we will be using the following notations wherever it is appropriate:

- \( \alpha, \beta, \xi, \) etc. – lower-case Greek letters for scalars.
- \( a, b, x, \) etc. – lower-case Latin letters for column vectors in particle space.

These vectors have \( n \) components.
• $A, B, X$, etc. – upper-case Latin letters for matrices in particle space. These are $n \times n$ matrices.

• $\alpha, \beta, a_i, b_j$, etc. – bold font for 3-dimensional vectors.

• $X', x'$, etc. – the prime stands for matrix (vector) transpose.

• $X^*, x^*, \xi^*$, etc. – the star stands for the complex conjugate. If applied to a matrix (vector) then there is no transposition assumed, i.e. the result is a matrix (vector) whose elements are complex conjugated elements of the initial matrix (vector).

• $X^\dagger, x^\dagger$, etc. – the dagger stands for matrix (vector) transpose followed by complex conjugation.

• $X^{-1}$ – stands for the inverse matrix.

• $\diag X$ – stands for a matrix whose diagonal elements are equal to the corresponding diagonal elements of $X$ and all off-diagonal elements are zeros.

• $|X|$ – vertical bars stand for the determinant of a matrix. However, if the object in between vertical bars is a 3-dimensional vector or a scalar then the absolute value of the vector (scalar) is assumed.

• $\tr X$ – stands for the trace of matrix $X$.

• $X \otimes Y$ – stands for the Kronecker product of matrices $X$ and $Y$.

For some quantities the above mentioned notation scheme will not be valid, but there should not be any confusion in those cases.

We also want to introduce two operators, vec and vech. They both transform a matrix into a vector. The vec operator stacks the columns of a matrix, one underneath the other. If $X$ is an $n \times n$ matrix with elements $X_{ij}$, then vec $X$ is the
following $n^2$-component vector:

\[
\begin{pmatrix}
X_{11} \\
X_{12} \\
\vdots \\
X_{1n} \\
X_{21} \\
\vdots \\
X_{nn}
\end{pmatrix}
\]

(2.9)

Unlike vec, the vech operator takes only the part of a column, that is beneath the diagonal, including the diagonal element. Hence, it results in a $n(n+1)/2$-component vector. For example, if $X$ is a $3 \times 3$ matrix, then

\[
\begin{pmatrix}
X_{11} \\
X_{12} \\
X_{13} \\
X_{22} \\
X_{23} \\
X_{33}
\end{pmatrix}
\]

(2.10)

In the case when matrix $X$ is symmetric, vech $X$ contains only its independent elements.

Let us list a few useful properties of vec and vech operators. If $X$ and $Y$ are arbitrary complex square matrices, and $L$ is a complex lower triangular matrix then

\[
(vec X)' vec Y = tr[X'Y],
\]

(2.11)

\[
(vec X)' vec L = (vech X)' vech L.
\]

(2.12)

For the case when both $X$ and $Y$ are complex symmetric or antisymmetric we have the following relationship:

\[
(vec X)' vec Y = (vech(2X - \text{diag} X))' vech Y.
\]

(2.13)
2.3 Variational method

The variational method is one of the most popular approaches in applied mathematics used to find approximate solutions of boundary value and eigenvalue problems. Though it gives only an approximate solution, one can get virtually exact results provided an appropriate choice of function space is made. In quantum mechanics our goal is to find approximate solutions of the time-independent Schrödinger equation,

$$\hat{H}\psi_i = E_i\psi_i,$$  \hspace{1cm} (2.14)

where, $E_i$ is the energy of state $i$, $\psi_i$ is the corresponding wave function, and index $i$ denotes a certain set of quantum numbers.

The Ritz theorem states that for an arbitrary trial function $\Psi$ that have the same symmetry as the ground state wave function the expectation value of the Hamiltonian is such that

$$E \equiv \langle \Psi | \hat{H} | \Psi \rangle \geq E_1.$$ \hspace{1cm} (2.15)

Here, $E_1$ is the energy of the ground state. Function $\Psi$ may have a certain number of parameters that give it flexibility to approach the exact wave function. By varying these parameters one can obtain an approximate solution for the ground state.

In practice it has proven to be very convenient and efficient to expand the wave function as a linear combination of certain basis function (again, these basis functions should have proper symmetry):

$$\Psi = \sum_{k=1}^{K} c_k \varphi_k.$$ \hspace{1cm} (2.16)

This is so called Ritz scheme. Linear coefficients $c_k$, as well as any nonlinear coefficient that functions $\varphi_k$ may contain, are chosen in such a way that the expectation value of the total energy is minimized. If $K \to \infty$, and the set of functions $\varphi_k$ is complete, then one should get the exact ground state energy. The problem of choosing coefficients $c_k$ is conveniently reduced to the generalized eigenvalue problem:

$$Hc = \epsilon Sc,$$ \hspace{1cm} (2.17)
with $H$ and $S$ being $\mathcal{K} \times \mathcal{K}$ matrices of the Hamiltonian and the overlap respectively, and $c$ being the column vector of coefficients $c_k$. The elements of $H$ and $S$ are:

$$H_{kl} = \langle \varphi_k | \hat{H} | \varphi_l \rangle, \quad S_{kl} = \langle \varphi_k | \varphi_l \rangle.$$  \hfill (2.18)

The above mentioned scheme is easily extended to consideration of excited states. The ground for this is so called mini-max theorem. It says that not only the lowest $\epsilon$ is the upper bound to the ground state energy, but all the roots of the equation (2.17) are the corresponding upper bounds to the excited states, i.e.

$$\epsilon_1 \geq E_1, \; \epsilon_2 \geq E_2, \; \ldots, \; \epsilon_K \geq E_K.$$

It is assumed above that all $\epsilon_j$ are ordered in such a way that $\epsilon_1 \leq \epsilon_2 \leq \ldots \leq \epsilon_K$.

For comprehensive and mathematically rigorous consideration of the theory of variational methods the reader is referred to numerous textbooks and monographs. In particular, for physicists interested in quantum mechanical few-body problems, we can recommend the monograph of Varga and Suzuki [9] that has a reasonably concise theory section.

### 2.4 Choice of basis functions

It is quite obvious that the quality of the variational expansion (2.16) crucially depends on the choice of basis functions. Even though, generally, one can use any function set from the class of allowed functions (i.e. those functions that satisfy necessary boundary conditions, that are square integrable, etc.), there are purely technical restrictions. Firstly, it is necessary that these functions be flexible enough to approximate the wave functions of the systems under consideration. Secondly, their matrix elements must be calculable with reasonable amount of effort (both in “analytical” and “numerical” sense). It should be noted that the degree of accuracy required from non-BO calculations is typically very high as the effects due to coupling between electronic and nuclear motions are relatively small. Thus, the correlations in the motion of all particles need be very well described. To achieve this,
the trial wave function has to depend on interparticle distances, $R_{ij}$ (or related coordinates, such as the Jacobi coordinates, or pseudoparticle coordinates introduced before).

Despite the variety of the explicitly correlated basis function types that can be imagined, only a few have practical applicability. One of these types is a family of explicitly correlated Gaussians. They have become very popular in variational calculations of various few-particle quantum mechanical systems in last several decades. The use of these functions represents a relatively simple yet very powerful tool for obtaining highly accurate solutions of the Schrödinger equation. The advantage of using Gaussians in comparison with other basis functions is that all basic matrix elements with Gaussians can be evaluated analytically for an arbitrary number of particles. At the same time, for most other explicitly correlated basis functions such a procedure often leads to rather complicated integrals that are either very hard or impossible to evaluate and implement numerically once one goes beyond systems containing three-four particles. As far as quantum chemical applications is concerned, explicitly correlated Gaussians were first introduced there by Boys [10] and Singer [11]. In this dissertation we will focus exclusively on explicitly correlated Gaussians. We will consider in details the types of correlated Gaussians, which have been used in the calculations that make up the core of the research summarized in this dissertation.

For atomic calculations of $s$-states, and calculations of any systems where the density of (pseudo)particles is not highly localized around more than one point in coordinate space the following form of Gaussians is applicable:

$$
\phi_k = \exp[-r' A_k r].
$$

Here $A_k$ is $n \times n$ real matrix. The lower index $k$ reflects the fact that this matrix is unique for each basis function. Although matrices $A_k$ do not have to be symmetric, one can always rearrange their elements, without changing the quadratic form itself, in such a way that they will be symmetric. This reduces the number of independent parameters and everywhere below we will be assuming that all $A_k$’s (and similar
matrices that appear in other basis functions) are symmetric. Quantum mechanics requires the total wave function to be finite and square integrable. This imposes a restriction on $A_k$. It must be positive definite. To assure the positive definiteness of $A_k$ it is very convenient to represent it as a Cholesky decomposition, $A_k = L_kL_k^T$, with $L_k$ being a lower triangular matrix. The advantage of such a representation is that there are no restrictions on the elements of $L_k$. Hence, if the numerical optimization of the elements is to be performed, we can safely use very efficient algorithms for a non-constrained optimization.

The above basis function is a one-center correlated Gaussian that corresponds to zero total angular momentum. It is a rotationally invariant function as required by the symmetry of the problem – that is, invariant with respect to any orthogonal transformation. To show the invariance let $U$ be any $3 \times 3$ orthogonal matrix (any proper or improper rotation in 3 space) that is applied to rotate the $r$ vector in the 3D space. Prove the invariance:

$$((I_n \otimes U)r)' (A_k \otimes I_3) (I_n \otimes U) r = r' (I_n \otimes U') (A_k \otimes I_3) (I_n \otimes U) r$$

$$= r' (A_k \otimes U'U) r = r' (A_k \otimes I_3) r.$$

The $n$-pseudoparticle one-center correlated Gaussian (2.19) can also be expressed in the more conventional form used in the electronic structure calculations as:

$$\phi_k = \exp \left[ -\alpha_{1k} r_1^2 - \alpha_{2k} r_2^2 - \ldots - \alpha_{nk} r_n^2 - \beta_{12,k} r_{12}^2 - \beta_{13,k} r_{13}^2 - \ldots - \beta_{nn-1,k} r_{nn-1}^2 \right].$$

(2.20)

In this form, the $n$-pseudoparticle correlated Gaussian is a product of $n$ orbital Gaussians centered at the origin of the coordinate system and $n(n-1)/2$ Gaussian pair functions (geminals).

Basis functions (2.19) have proven to be very effective in atomic calculations. However, in case of molecular systems the situation is more complicated than in atoms. Non-Born–Oppenheimer calculations of, for example, pure vibrational states require that the basis functions accurately represent the nodes in the wave function that occur along the relative nucleus–nucleus coordinates. Since nuclei are highly localized around their equilibrium positions and they are much heavier than the
electrons, the vibrational component of the total wave function has sharp peaks. In a diatomic system described in an internal coordinate frame with one of the nuclei at the coordinate origin (this is the frame we use) those peaks are shifted away from the origin. However, simple one-center Gaussians have their peaks at the origin, where the vibrational component of the wave function has to have an extremely low amplitude. There have been proposed different ways to overcome this difficulty. The first is to use Gaussians with shifted centers (see references [12, 13, 14] for examples of such calculations). The basis functions in this case look as follows:

$$\varphi_k = \exp \left[ -(r - s_k') A_k (r - s_k) \right],$$  \hspace{1cm} (2.21)

where $s_k$ are some $3n$-component vectors (shifts) that are, in general, different for each basis function and should be optimized like the elements of matrices $A_k$. Even though shifted Gaussians are applicable in some cases, the problem here is that these basis functions are not eigenfunctions of the total angular momentum operator. Thus, calculations of vibrationally excited states are intrinsically problematic.

Another way to attack molecular systems is to modify Gaussians by including premultipliers in the form of powers of the internuclear distances as was first done for diatomics in [6, 15]. If we deal with a diatomic system then this premultiplier consists of only one internuclear distance raised to some even power:

$$\varphi_k = r_1^{m_k} \exp \left[ -r' A_k r \right].$$  \hspace{1cm} (2.22)

For technical reasons, as will be explained later, powers $m_k$ are restricted to be even integers. The range of values of $m_k$ depends on the system and typically needs to be quite wide, 0–200 or even higher. Basis functions (2.22) turned out to be very efficient in calculations of small diatomic molecular systems [6, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31]. In fact, the major part of the calculations presented in this dissertation are done using these “diatomic” basis functions.

Basis set (2.22) works quite well in the case of diatomic systems. However, the generalization of this approach to triatomic systems encounters serious problems with obtaining compact analytical expressions for matrix elements and not less serious problems with practical implementation [32].
There is yet another way of describing the radial nodes in the ground and excited state wave functions of atomic and molecular systems calculated in non-Born–Oppenheimer mode. The approach is based on the use of explicitly correlated Gaussian functions with complex exponential parameters. Such functions are much more flexible than real Gaussians and, put together in certain combinations (to simulate periodic functions such as sin or cos they should be capable of providing a good description of the radial oscillations in the wave function in atomic and molecular excited states. Another application of complex Gaussians may be calculations of quantities whose matrix elements are difficult to evaluate with Gaussians containing premultipliers in the form of powers of internuclear distances.

Despite the simplicity of the idea of using complex parameters in Gaussians, it has received almost no attention in the literature. The use of complex parameters has been done in calculations of three- and four-particle systems with the Slater-type basis functions [33, 34, 35, 36]. As far as complex Gaussians are concerned, except for one simple calculation of a few four-particle systems [37], there has not been much more done in this area, according to our knowledge.

The form of complex Gaussian functions is the following:

\[ \phi_k = \exp \left[ -r'(A_k + iB_k)r \right] \equiv \exp \left[ -r'C_k r \right]. \]  \hfill (2.23)

Here \( A_k \) and \( B_k \) are \( n \times n \) real matrices. Sometimes it is convenient to use one complex matrix instead, which we will denote \( C_k \). Notice that, unlike the elements of \( A_k \), the elements of \( B_k \) may, in principle, take any values as this does not affect the positive definiteness of \( C_k \). Thus, the use of Cholesky decomposition for \( B_k \) does not provide any advantages.

The calculations presented in this dissertation are primarily done using functions (2.22) and (2.23). Thus, in the next chapters we will focus on the derivations of necessary matrix elements with these basis functions.
2.5 Permutational symmetry

In many practical situations atomic or molecular systems contain some subsets of identical particles. These can be electrons, identical nuclei, and even exotic particles such as positrons or muons. According to the Pauli principle, the total wave function of such systems (including spin degrees of freedom) must be either symmetric or antisymmetric with respect to permutation of the identical particles. As the result of this requirement, the basis functions used in variational calculations also should (in most cases must) possess certain permutational symmetry. If we deal with Hamiltonians that do not depend on spin then the total wavefunction is a product of spatial and spin parts. In the same way one should build the basis functions. The spatial parts of basis functions multiplied by the spin part need be either totally symmetric or totally antisymmetric under permutation of identical particles. However, if we consider only spatial or spin part separately, their structure is more complicated. Even though their product is totally symmetric or totally antisymmetric, none of them, in general (unless we deal with systems that contain no more than two identical particles of the same kind), are totally symmetric or antisymmetric. The spatial parts of the basis functions need be eigenfunctions of some representations of certain symmetric groups that correspond to “mixed” symmetry. These representations are, in general, multidimensional, and, thus, if the Hamiltonians were spin-dependent we would have to deal with several sets of basis functions (more precisely with several components of eigenfunctions). Luckily, in the case of spin-independent Hamiltonians, this procedure is greatly simplified. We can pick any single component and use it as they are all equivalent in terms of the energy or other quantities that we usually want to calculate. The role of the spin part of the basis functions is rather formal. It is only needed to keep the proper symmetry of the product with the spatial part, but as such it does not make any difference in calculating properties we want to know as long as the Hamiltonian is spin-independent.

Generation of basis functions (their spatial parts) that obey correct permuta-
tional symmetry can be done by projecting some primitive basis functions, that, in general, do not have any symmetry, such as functions (2.22) or (2.23), onto subspace of eigenfunctions of certain irreducible representations of the symmetric group. This procedure described in details in the book on group theory by Morton Hamermesh [38]. We will only present here a short description of it that is sufficient for our applications.

The method we use to build basis functions of proper symmetry is based on using Young operators, \( \hat{Y} \). For simplicity we will assume that there is only one kind of identical particles in the system. The generalization to systems with several kinds of identical particles is quite obvious in most cases (though sometimes the symmetry of a system containing more than one kind of identical particles may be more complicated). The Young operators applied to primitive basis functions leave only the component of desired symmetry. The general form of the Young operator is:

\[
\hat{Y} = \prod_{j=1}^{n_j} \hat{A}_j \prod_{i=1}^{n_i} \hat{S}_i.
\]  
(2.24)

Operators \( \hat{S}_i \) and \( \hat{A}_j \) are symmetrizers and antisymmetrizers over certain subsets of the identical particles in the systems. They are easily obtainable from consideration of Young frames. A Young frame is a series of connected boxes such as

\[
\begin{array}{ccc}
1 & 2 & 3 \\
4 & 5 \\
6
\end{array}
\]

where numbers are used to mark particles. The shape of the Young frame corresponding to the desired irreducible representation of the symmetric group is obtained from the physics of the system. For the totally symmetric representation of the \( k \)-th order symmetric group we use a frame that is completely horizontal with \( k \) boxes. For example, for 5 particles we have:
For the totally antisymmetric representation of the $k$-th order symmetric group we use a frame that is completely vertical with $k$ boxes. In the case of 3 particles it looks as follows:

\[
\begin{array}{ccccc}
1 & 2 & 3 & 4 & 5 \\
\end{array}
\]

It should be noted that numbering of boxes is up to the user. Although different ways of numbering boxes may lead to different Young operators, all of them are equivalent in terms of the such properties of the system as energy and other expectation values. In other words, if the user carries out a calculation using one Young operator (generates a basis set, optimizes nonlinear parameters, etc.), then another calculation with another Young operator done in the same way (with the same number of basis functions and the same amount of work spent on the linear parameter optimization) should yield similar in accuracy results. In fact, this is a reflection of indistinguishability of particles as such: no matter how one numbers them, the outcome should be independent of this numbering.

In most practical situation we have to deal with identical particles that are either spin 1/2 fermions (an example would be electrons) or bosons. For bosons, the spatial part of the wave function of the states with the lowest energy corresponds to Young frames that are completely horizontal. For spin 1/2 fermions, the symmetry of the spatial part of the wave function is dictated by Young frames that have two columns. The examples of such frames in the case of 2, 5, and 6 particles are given below:

\[
\begin{array}{cc}
1 & 2 \\
3 & 4 \\
5 \\
\end{array}
\quad
\begin{array}{cc}
1 & 2 \\
3 & 4 \\
5 & 6 \\
\end{array}
\]
Now let us return to the general form of the Young operator (2.24). \( n_i \) and \( n_j \) in (2.24) are the number of rows and number of columns in the Young frame respectively. \( \hat{S}_i \) is the symmetrizer over all particles in row \( i \) and \( \hat{A}_j \) is antisymmetrizer over all particles in column \( j \). The symmetrizers and antisymmetrizers can be conveniently represented by compact expressions that involve transpositions (pair permutations of particles), which we will denote \( \hat{P}_{kl} \). For example, if we have 2 particles whose numbers are 1 and 2 then the symmetrizer is

\[
\hat{S} = 1 + \hat{P}_{12}. \tag{2.25}
\]

The antisymmetrizer over particles 1 and 2 also has a simple form:

\[
\hat{A} = 1 - \hat{P}_{12}. \tag{2.26}
\]

For the sake of simplicity we dropped the normalization factor in both expressions above as it not essential at this point. In the case of larger than 2 number of particles over which the symmetrization or antisymmetrization needs to be done the corresponding expressions can be given in factorized form. Let us assume that the number of particles in a subset is \( k \) and their numbers range from 1 to \( k \). Then the symmetrizer and antisymmetrizer would look as follows:

\[
\hat{S} = (1 + \hat{P}_{12})(1 + \hat{P}_{13} + \hat{P}_{23}) \ldots (1 + \hat{P}_{1k} + \ldots + \hat{P}_{k-1,k}). \tag{2.27}
\]

\[
\hat{A} = (1 - \hat{P}_{12})(1 - \hat{P}_{13} - \hat{P}_{23}) \ldots (1 - \hat{P}_{1k} - \ldots - \hat{P}_{k-1,k}). \tag{2.28}
\]

Again, the normalization factors \((1/\sqrt{k!})\) were dropped for convenience. For illustration purpose let us build the Young operator for the case of 5 identical particles with spin 1/2 (electrons). The corresponding Young frame for this set of particles (assuming their numbers range from 1 to 5) is

\[
\begin{array}{cc}
1 & 2 \\
3 & 4 \\
5 & \\
\end{array}
\]
We symmetrize over rows 1 and 2 by applying $1 + \hat{P}_{12}$ and $1 + \hat{P}_{34}$. Then we antisymmetrize over columns 1 and 2 by means of operators $(1 - \hat{P}_{13})(1 - \hat{P}_{15} - \hat{P}_{35})$ and $1 - \hat{P}_{24}$. Thus, the entire Young operator is the following:

$$\hat{Y} = (1 - \hat{P}_{24})(1 - \hat{P}_{13})(1 - \hat{P}_{15} - \hat{P}_{35})(1 + \hat{P}_{12})(1 + \hat{P}_{34}).$$

Knowing how to obtain the Young operators we now need to consider how operators of pair permutations of particles act on primitive basis functions (2.22) and (2.23).

The permutations of real particles induce transformations on internal coordinates, $r_i$. These transformations are linear, as the connection between the laboratory coordinates, $R_i$, and the internal coordinates is linear. In the case of complex or real one-center Gaussian basis functions, the action of a permutational operator, $\hat{P}$ (which may be a simple transposition or, more generally, a product of transpositions), can be conveniently represented by the corresponding permutational matrix, $P$:

$$\hat{P} \exp[-r'C_i r] = \exp[-(Pr')^tC_i (Pr)] = \exp[-r'(P'C_i P)r].$$

As one can see, with the action of the permutational operator the matrix of nonlinear parameters, $C_l$, undergoes a similarity transformation. It should be noted that matrix $P$ is not in general an elementary transformation matrix. The explicit form of $P$ depends on the operator $\hat{P}$. In the case of a transposition it has a very simple view. If the transposition involves particle 1 (i.e. the reference particle) and $j$, then the corresponding matrix $P$ for internal coordinate transformation is an $n \times n$ identity matrix with all elements in the $j$-th column replaced by $-1$. For transpositions that involve particles $i$ and $j$ (and neither one is particle 1) the matrix is the identity matrix with interchanged columns $(i - 1)$ and $(j - 1)$, as well as rows $(i - 1)$ and $(j - 1)$.

The important consequence of the aforementioned is the fact that the calculation of all matrix elements with complex Gaussians affected by permutational operators is no different from the case when the Gaussians are not affected. One just needs to transform the matrices of nonlinear variational parameters, $C_l$, accordingly.
Diatomic basis functions (2.22) are transformed in the same manner as one-center real or complex gaussians. This is because they differ by a premultiplier in the form of a power of $|r_1| = |R_2 - R_1|$. It is easy to see that this distance does not change under action of $\hat{P}_{12}$, which is permutation of nuclei (particles 1 and 2). On the other hand, if particles 1 and 2 are the only nuclei, then there are no other identical particles of the same type in the system, and, hence, there may not be transpositions like $\hat{P}_{1i}$ or $\hat{P}_{2i}$ in the Young operator.

As a rule, the operators whose matrix elements are required in variational calculations of a quantum mechanical system commute with all the permutations from the permutational symmetry group of that system. Due to this fact the matrix elements of an operator, $\hat{O}$, can be written in the following way:

$$\langle \phi_k | \hat{Y}^\dagger \hat{O} \hat{Y} | \phi_l \rangle = \langle \phi_k | \hat{O} \hat{Y}^\dagger \hat{Y} | \phi_l \rangle.$$ (2.31)

Thus, in our derivations we may restrict ourselves to the case when only the ket is affected by the permutation operators.

In the end of this section we would like to make a note regarding the evaluation and efficient implementation of the action of $\hat{Y}^\dagger \hat{Y}$ operator in (2.31). If a system contains $k$ identical particles of some type then the corresponding Young operator has $k!$ terms. The expression for $\hat{Y}^\dagger \hat{Y}$ then has $k!^2$ terms. However, they are not all independent. In fact, $\hat{Y}^\dagger \hat{Y}$ contains the same permutations as $\hat{Y}$ does, but the coefficients by these permutations may be different. Therefore, to avoid a large amount of unnecessary calculations it is important to reduce $\hat{Y}^\dagger \hat{Y}$ to a linear combination of inequivalent permutations. Doing this manually in the case when the number of particles is larger than three or four becomes a tedious task. A better approach is to implement this simplification procedure in the computer code, which is executed every time before the main phase of calculations is started.

2.6 Matrix elements with complex Gaussians

In this section we will derive various matrix elements with complex Gaussians (2.23) that are needed in variational calculations of Coulombic systems. Since real, one-
center, Gaussians are a partial case of complex Gaussians, we will also automatically obtain many necessary expressions for the former ones. Some of these matrix elements will be used in the next section, where we will consider matrix elements over Gaussians with premultipliers (2.22).

To begin let us first give the value of a well-known Gaussian integral, which will be used in the derivations below:

\[
\int_{-\infty}^{+\infty} \exp \left[-x'Cx + y'x\right] \, dx = \frac{\pi^{n/2}}{|C|^{1/2}} \exp \left[\frac{1}{4}y'\left(C^{-1}y\right)\right].
\] (2.32)

The integration here is over \( n \) variables, and \( x \) is an \( n \)-component vector of these variables. \( y \) is a constant vector, \( n \times n \) matrix \( C \) is assumed to be symmetric, and its real part is positive definite. Also, here and everywhere below, by the square root one should understand its principal value (i.e. that root whose real part is greater than zero).

The following notations will help keep expressions more compact:

\[
|\tilde{\phi}_l\rangle = \hat{P}|\phi_l\rangle,
\] (2.33)

\[
\tilde{L}_k = P'L_k, \quad \tilde{A}_k = P'A_kP, \quad \tilde{B}_k = P'B_kP,
\] (2.34)

\[
A_{kl} = A_k + A_l, \quad \tilde{A}_{kl} = A_k + \tilde{A}_l,
\] (2.35)

\[
B_{kl} = -B_k + B_l, \quad \tilde{B}_{kl} = -B_k + \tilde{B}_l,
\] (2.36)

and

\[
\tilde{C}_{kl} = C_k^* + \tilde{C}_l = \tilde{A}_{kl} + i\tilde{B}_{kl}.
\] (2.37)

Here \( P \) represents the permutation matrix corresponding to some permutation operator, \( \hat{P} \).
2.6.1 Overlap

The overlap integral follows directly from formula (2.32). We just need to keep in mind that the integration is done over $3n$ variables:

$$
\langle \phi_k | \tilde{\phi}_l \rangle \equiv \langle \phi_k | \tilde{P} | \phi_l \rangle = \int_{-\infty}^{+\infty} \exp[-r' C_k^* r^\prime] \tilde{P} \exp[-r' C_l r] \, d \mathbf{r}
$$

$$
= \int_{-\infty}^{+\infty} \exp[-r' C_k^* r] \exp[-r' \tilde{C}_l r] \, d \mathbf{r} = \frac{\pi^{3n/2}}{|\tilde{C}_{kl}|^{3/2}}.
$$

(2.38)

For the overlap matrix elements with normalized basis functions, which are superior in practical calculations, we have:

$$
S_{kl} \equiv \frac{\langle \phi_k | \tilde{\phi}_l \rangle}{(\langle \phi_k | \phi_k \rangle \langle \phi_l | \phi_l \rangle)^{1/2}} = \frac{\langle C_{kk} | C_{ll} \rangle^{3/2} |C_{kl}|^{3/2}}{|\tilde{C}_{kl}|^{3/2}} = 2^{3n/2} \left( \frac{|L_k| |L_l|}{|\tilde{C}_{kl}|} \right)^{3/2}.
$$

(2.39)

2.6.2 Kinetic energy

As one can easily verify, the action of the $\nabla_r$ operator on the basis functions is as follows:

$$
\nabla_r \phi_k = -2\phi_k C_k r.
$$

(2.40)

Using this result we can obtain the following expression for the kinetic energy operator matrix elements:

$$
\langle \phi_k | - \nabla_r^\dagger M \nabla_r | \tilde{\phi}_l \rangle = \langle \nabla_r \phi_k | M | \nabla_r \tilde{\phi}_l \rangle
$$

$$
= 4\langle C_k r \phi_k | M | \tilde{C}_l r \tilde{\phi}_l \rangle = 4\langle \phi_k | r' C_k^\dagger M \tilde{C}_l r | \tilde{\phi}_l \rangle
$$

$$
= 4\langle \phi_k | \text{tr} \left[ r r' C_k^\dagger M \tilde{C}_l \right] | \tilde{\phi}_l \rangle = 4\langle \phi_k | \text{vec} (r r')' | \tilde{\phi}_l \rangle \text{vec}(C_k^\dagger M \tilde{C}_l).
$$

(2.41)
The first factor here is:

\[
\langle \phi_k | \text{vec} (rr') | \tilde{\phi}_l \rangle = \int_{-\infty}^{\infty} \phi_k^* \text{vec} (rr') \tilde{\phi}_l \, dr = \int_{-\infty}^{\infty} \frac{\partial \phi_k^* \tilde{\phi}_l}{\partial \text{vec}(C_{kl})'} \, dr
\]

\[
= - \frac{\partial}{\partial \text{vec}(\tilde{C}_{kl})'} \int_{-\infty}^{\infty} \phi_k^* \tilde{\phi}_l \, dr = - \frac{\partial}{\partial \text{vec}(\tilde{C}_{kl})'} \frac{\pi^{3n/2}}{2} \frac{|C_{kl}|^{3/2}}{\partial \text{vec}(C_{kl})'}
\]

\[
= \frac{3}{2} \frac{\pi^{3n/2}}{|C_{kl}|^{5/2}} |\tilde{C}_{kl}| \text{vec}(\tilde{C}_{kl}^{-1})' = \frac{3}{2} \langle \phi_k | \tilde{\phi}_l \rangle \text{vec}(\tilde{C}_{kl}^{-1})'.
\]

Above we used the facts that for an arbitrary matrix \(X\),

\[
d |X| = |X| \text{tr} [X^{-1}dX] = |X| \text{vec} ((X^{-1})') \text{vec}(dX),
\]

\[
\frac{\partial |X|}{\partial \text{vec} (X)'} = |X| \text{vec} ((X^{-1})'),
\]

and that matrix \(\tilde{C}_{kl}^{-1}\) is symmetric.

Thus,

\[
\langle \phi_k | - \nabla_r' M \nabla_r | \tilde{\phi}_l \rangle = 6 \langle \phi_k | \tilde{\phi}_l \rangle \text{vec}(\tilde{C}_{kl}^{-1})' \text{vec}(C_{kl}^\dagger M \tilde{C}_{kl})
\]

\[
= 6 \langle \phi_k | \tilde{\phi}_l \rangle \text{tr} [\tilde{C}_{kl}^{-1} C_{kl}^\dagger M \tilde{C}_{kl}] = 6 \langle \phi_k | \tilde{\phi}_l \rangle \text{tr} [M \tilde{C}_{kl} \tilde{C}_{kl}^{-1} C_{kl}^\dagger].
\]

In case of normalized basis functions the kinetic energy matrix element becomes:

\[
T_{kl} = 6 S_{kl} \text{tr} [M \tilde{C}_{kl} \tilde{C}_{kl}^{-1} C_{kl}^\dagger].
\]

2.6.3 Pair correlation function and potential energy

In the beginning let us obtain an auxiliary formula, which will be very useful in further derivations. The formula is for the matrix element of the 3-dimensional Dirac delta function,

\[
\delta(a' r - \boldsymbol{\xi}) = \delta(a_1 r_1 + a_2 r_2 + \ldots + a_n r_n - \boldsymbol{\xi}),
\]

where \(a\) is a real \(n\)-component vector, and \(\boldsymbol{\xi}\) is some real 3-dimensional parameter.
Using the following representation of the delta function,
\[
\delta(a'r - \xi) = \lim_{\beta \to \infty} \left(\beta \pi\right)^{3/2} \exp \left[-\beta(a'r - \xi)^2\right],
\] (2.47)
and formula (2.32) we have:
\[
\langle \phi_k | \delta(a'r - \xi) | \tilde{\phi}_l \rangle = \lim_{\beta \to \infty} \left(\frac{\beta}{\pi}\right)^{3/2} \langle \phi_k | \exp \left[-\beta(\tilde{C}_{kl} + \beta a' a^\dagger) - 1 a \xi - \beta \xi^2\right] | \tilde{\phi}_l \rangle.
\] (2.48)

Since \(a a'\) is a rank one matrix we can write the determinant in the last formula as
\[
| \tilde{C}_{kl} + \beta a a' | = | \tilde{C}_{kl} | I + \beta \tilde{C}_{kl}^{-1} a a' | = | \tilde{C}_{kl} | (1 + \beta \text{tr}[\tilde{C}_{kl}^{-1} a a'])
\] (2.49)
where \(I\) is \(n \times n\) identity matrix. Indeed, matrix \(\tilde{C}_{kl}^{-1} a a'\) has rank one and its only non–zero eigenvalue is \(\text{tr}[\tilde{C}_{kl}^{-1} a a']\), since the trace of a matrix is the sum of its eigenvalues. Adding the identity matrix just increases all the eigenvalues by one. Hence, the eigenvalues of \(I + \beta \tilde{C}_{kl}^{-1} a a'\) are \(1 + \beta \text{tr}[\tilde{C}_{kl}^{-1} a a']\) and ones. Since the determinant is the product of all eigenvalues, we have what is given in (2.49).

As the limit of the preexponential part in (2.48) is a finite number, the limit of the expression in the exponent must be equal to \(-\gamma \xi^2\), with \(\gamma\) being a finite number. Otherwise the entire expression (2.48) would have had its limit equal to either zero or infinity, which is not the case. Hence,
\[
\langle \phi_k | \delta(a'r - \xi) | \tilde{\phi}_l \rangle = \frac{\pi^{3(n-1)/2}}{| \tilde{C}_{kl} |^{3/2} \text{tr}[\tilde{C}_{kl}^{-1} a a']^{3/2}} \exp[-\gamma \xi^2]
\]
\[
= \langle \phi_k | \delta(a'r - \xi) | \tilde{\phi}_l \rangle = \frac{\pi^{3/2}}{| \tilde{C}_{kl} |^{3/2} \text{tr}[\tilde{C}_{kl}^{-1} a a']^{3/2}} \exp[-\gamma \xi^2].
\] (2.50)

Making use of the normalization condition,
\[
\int_{-\infty}^{\infty} \langle \phi_k | \delta(a'r - \xi) | \tilde{\phi}_l \rangle \, d\xi = \langle \phi_k | \tilde{\phi}_l \rangle,
\] (2.51)
we can find that \( \gamma = \text{tr}[\tilde{C}^{-1}_{kl}aa']^{-1} \). Thus,

\[
\langle \phi_k | \delta(a' r - \xi) | \tilde{\phi}_l \rangle = \langle \phi_k | \tilde{\phi}_l \rangle \frac{1}{\pi^{3/2}} \frac{1}{\text{tr}[\tilde{C}^{-1}_{kl}aa']^{3/2}} \exp \left[ -\frac{\xi^2}{\text{tr}[\tilde{C}^{-1}_{kl}aa']} \right].
\] (2.52)

Let us now derive the expression for the matrix elements of the pair correlation function,

\[
g^{ij}(\xi) \equiv \langle \psi | \delta(r_{ij} - \xi) | \psi \rangle \quad \text{(2.53)}
\]

\[
g^{i}(\xi) \equiv \langle \psi | \delta(r_i - \xi) | \psi \rangle , \quad \text{(2.54)}
\]

which in case (2.53) is the probability density of pseudoparticles \( i \) and \( j \), or, equivalently, particles \( i+1 \) and \( j+1 \) to have separation \( \xi \). Expression (2.54) is used when the pair correlation function of particles 1 and \( i+1 \) is needed. Here, \( \psi \) is the wave function of the system under consideration. Apart from being a useful quantity itself, the correlation function (2.53, 2.54) will serve as an auxiliary tool to obtain the expression for the potential energy and any other quantity that depends on \( r_i \) or \( r_{ij} \). To help preserve all the derivations in the matrix form, we will introduce vector \( j^i \) whose only non–zero component is the \( i \)-th one, which is equal to one. Also, we will introduce a rank one matrix \( J_{ij} \). Its definition is as follows:

\[
J_{ij} = \begin{cases} 
E_{ii} & \text{if } i = j \\
E_{ii} + E_{jj} - E_{ij} - E_{ji} & \text{if } i \neq j 
\end{cases}
\] (2.55)

where \( E_{ij} \) is a matrix with 1 in the \( i, j \)-th position and 0’s elsewhere.

Noticing that \( r_{ij} = (j^j - j^i)'r, \ r_i = (j^i)'r, \) and also \( (j^j - j^i)(j^j - j^i)' = J_{ij} \) for \( i \neq j, \ j^i(j^i)' = J_{ii} \) we can easily conclude that,

\[
\langle \phi_k | \delta(r_{ij} - \xi) | \tilde{\phi}_l \rangle = \langle \phi_k | \tilde{\phi}_l \rangle \frac{1}{\pi^{3/2}} \frac{1}{\text{tr}[\tilde{C}^{-1}_{kl}J_{ij}]^{3/2}} \exp \left[ -\frac{\xi^2}{\text{tr}[\tilde{C}^{-1}_{kl}J_{ij}]} \right],
\] (2.56)

and

\[
\langle \phi_k | \delta(r_i - \xi) | \tilde{\phi}_l \rangle = \langle \phi_k | \tilde{\phi}_l \rangle \frac{1}{\pi^{3/2}} \frac{1}{\text{tr}[\tilde{C}^{-1}_{kl}J_{ii}]^{3/2}} \exp \left[ -\frac{\xi^2}{\text{tr}[\tilde{C}^{-1}_{kl}J_{ii}]} \right].
\] (2.57)
The above expressions for the matrix elements of the correlation function allows one to evaluate the matrix elements of an arbitrary function \(\chi(\vec{r}_{ij})\):

\[
\langle \phi_k | \chi(\vec{r}_{ij}) | \tilde{\phi}_l \rangle = \int_{-\infty}^{\infty} \chi(\vec{r}_{ij}) \langle \phi_k | \delta(\vec{r}_{ij} - \xi) | \tilde{\phi}_l \rangle \, d\xi
\]

\[
= \langle \phi_k | \tilde{\phi}_l \rangle \frac{1}{\pi^{3/2}} \frac{1}{\text{tr}[\tilde{C}_{kl}^{-1}J_{ij}]^{3/2}} \int_{-\infty}^{\infty} \chi(\xi) \exp \left[ -\frac{\xi^2}{\text{tr}[\tilde{C}_{kl}^{-1}J_{ij}]} \right] \, d\xi.
\]

(2.58)

If \(\chi(\vec{r}_{ij})\) depends only on the absolute value of the interpseudoparticle distance, this formula becomes:

\[
\langle \phi_k | \chi(\vec{r}_{ij}) | \tilde{\phi}_l \rangle = \langle \phi_k | \tilde{\phi}_l \rangle \frac{4}{\sqrt{\pi}} \frac{1}{\text{tr}[\tilde{C}_{kl}^{-1}J_{ij}]^{3/2}} \times \int_{0}^{\infty} \xi^2 \chi(\xi) \exp \left[ -\frac{\xi^2}{\text{tr}[\tilde{C}_{kl}^{-1}J_{ij}]} \right] \, d\xi.
\]

(2.59)

In particular, for \(\chi(\xi) = \xi^\nu\) with \(\nu\) being a real number, \(\nu > -3\), using the value of the integral:

\[
\int_{0}^{\infty} \lambda^\kappa e^{-\alpha \lambda^2} \, d\lambda = \frac{1}{2} \Gamma\left(\frac{\kappa+1}{2}\right) \quad \text{Re} \kappa > -1, \text{ Re} \alpha > 0,
\]

(2.60)

where \(\Gamma(\kappa)\) is the Euler gamma function, we obtain:

\[
\langle \phi_k | r_{ij}^{\nu} | \tilde{\phi}_l \rangle = \langle \phi_k | \tilde{\phi}_l \rangle \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{\nu+3}{2}\right) \text{tr} \left[\tilde{C}_{kl}^{-1}J_{ij}\right]^{\nu/2}.
\]

(2.61)

If \(\nu = -1\), as is the case for the Coulomb potential, then

\[
\langle \phi_k | \frac{1}{r_{ij}} | \tilde{\phi}_l \rangle = \langle \phi_k | \tilde{\phi}_l \rangle \frac{2}{\sqrt{\pi}} \frac{1}{\text{tr} \left[\tilde{C}_{kl}^{-1}J_{ij}\right]^{1/2}},
\]

(2.62)

and the corresponding expression with normalized basis functions is:

\[
R_{kl}^{ij} = \frac{2}{\sqrt{\pi}} S_{kl} \frac{1}{\text{tr} \left[\tilde{C}_{kl}^{-1}J_{ij}\right]^{1/2}},
\]

(2.63)

With this we can now write the expression for the potential energy matrix element, \(V_{kl}\), as follows:

\[
V_{kl} = \sum_{i=1}^{n} q_0 q_i R_{kl}^{ii} + \sum_{i<j}^{n} q_i q_j R_{kl}^{ij},
\]

(2.64)
or

$$V_{kl} = \frac{2S_{kl}}{\sqrt{n}} \left( \sum_{i=1}^{n} \frac{q_i q_i}{\text{tr} \left[ \tilde{C}_{kl}^{-1} J_{ii} \right]^{1/2}} + \sum_{i<j}^{n} \frac{q_i q_j}{\text{tr} \left[ \tilde{C}_{kl}^{-1} J_{ij} \right]^{1/2}} \right) .$$  (2.65)

For practical implementation it is useful to note that the trace of a product of an arbitrary matrix $X$ and $J_{ij}$ has a very simple form in terms of the elements of $X$:

$$\text{tr} [X J_{ij}] = \begin{cases} (X)_{ii} & \text{if } i = j \\ (X)_{ii} + (X)_{jj} - (X)_{ij} - (X)_{ji} & \text{if } i \neq j \end{cases} .$$  (2.66)

2.6.4 Particle density

The particle densities are tools for analyzing quantum mechanical systems of few particles since the wave function for such systems cannot be visualized due to its multidimensional nature. Below we present the matrix elements of this quantity evaluated with complex Gaussians.

If a system is described by wave function $\psi$, then the density of particle $i$ in the reference frame where the center of mass of the system, $r_0$, is at rest is given by the formula,

$$\rho^i(\xi) \equiv \langle \psi | \delta(R_i - r_0 - \xi) | \psi \rangle .$$  (2.67)

Here, $R_i$, expressed through internal coordinates, can be taken from (2.3). The calculation of the density using complex Gaussians requires the following matrix elements:

$$\langle \phi_k | \delta((b^i)' \cdot r - \xi) | \tilde{\phi}_l \rangle ,$$  (2.68)

where $b^i$ is an $n$-component vector whose elements in case when $i > 1$ are:

$$(b^i)_j = -M_{j+1}/m_0, \quad j = 1 \ldots n, \quad j \neq i - 1,$$

$$(b^i)_{i-1} = 1 - M_i/m_0 .$$

If $i = 1$, then the elements of $b^1$ are

$$(b^1)_j = -M_{j+1}/m_0, \quad j = 1 \ldots n .$$
In order to evaluate (2.68) we make use of the previously derived relation (2.52):

$$
\langle \phi_k | \delta \left((b^i)r - \xi\right) | \tilde{\phi}_l \rangle = \langle \phi_k | \tilde{\phi}_l \rangle \frac{1}{\pi^{3/2}} \frac{1}{\text{tr}[\tilde{C}^{-1}_{kl} b^i (b^i)^\dagger]^{3/2}} \exp \left[ -\frac{\xi^2}{\text{tr}[\tilde{C}^{-1}_{kl} b^i (b^i)^\dagger]} \right].
$$

(2.69)

In case of the normalized density matrix elements the latter expression becomes:

$$
\rho_{kl}^i(\xi) = \frac{1}{\pi^{3/2}} S_{kl} \frac{1}{\text{tr}[\tilde{C}^{-1}_{kl} b^i (b^i)^\dagger]^{3/2}} \exp \left[ -\frac{\xi^2}{\text{tr}[\tilde{C}^{-1}_{kl} b^i (b^i)^\dagger]} \right].
$$

(2.70)

### 2.6.5 General remarks regarding energy gradient

The formulae we derived above are sufficient for carrying out energy calculations and finding the wave functions. In principle, it is possible to write a computer code that performs such a task using only these formulae. However, if we aim for high precision in calculations, then many basis functions have to be included and the nonlinear parameters contained in these functions (elements of matrices $A_k$ and $B_k$) have to be optimized, as the accuracy of variational expansions in terms of correlated Gaussians strongly depends on the values of these parameters. The total number of nonlinear parameters may reach many thousands and their simultaneous optimization represents a very time consuming computational task. The use of the finite difference gradient of the energy as a function of nonlinear parameters is very costly and puts serious restrictions on the maximal number of basis functions. The utilization of the analytic gradient helps to relax this restriction and can speed up the calculation process by several orders of magnitude. Thus, the use of the analytic gradient is very important in many practical situations. Below we shortly describe the procedure of constructing the analytic gradient of the energy functional and derive necessary matrix elements.

### 2.6.6 Constructing the energy gradient

In the Rayleigh-Ritz variational scheme the wave function of the system under consideration, $\psi(r)$, is approximated as a linear combination of $K$ basis functions $\varphi_k$,

$$
\psi(r) = \sum_{k=1}^{K} c_k \varphi_k(r).
$$

(2.71)
The upper bounds, $\epsilon$, to the exact energies are then obtained from the solution of the secular equation,

$$\left(H - \epsilon S\right)c = 0, \quad (2.72)$$

where $H$ and $S$ are $K \times K$ hermitian matrices of the Hamiltonian and the overlap respectively, whose elements are $H = \langle \phi_k | \hat{H} | \phi_l \rangle$ and $S = \langle \phi_k | \phi_l \rangle$; $c$ is a $K$-component complex vector with elements $c_k$. We will be assuming that $\epsilon$ and $c$ correspond to a certain state (quantum number). This will keep the notations simple as we will not need to use any indices for $\epsilon$ and $c$ to denote the quantum number(s).

Taking the differential of (2.72),

$$d \left[ (H - \epsilon S)c \right] = (dH)c - (d\epsilon)Sc - \epsilon (dS)c + (H - \epsilon S)dc, \quad (2.73)$$

and multiplying by $c^\dagger$ from the left we obtain:

$$d \epsilon = c^\dagger (dH - \epsilon dS)c. \quad (2.74)$$

In the above expression we assumed that $c$ is normalized in such a way that $c^\dagger Sc = 1$. It is worth noting that relation (2.74) is essentially the same as the Hellmann-Feynman theorem. The differentiation in (2.74) may be performed with respect to any arbitrary variable, regardless of its nature. It does not matter whether the quantity is a physical parameter, for instance, a charge, or a variable that characterizes the trial wave function, such as a nonlinear variational parameter(s).

We can rewrite (2.74) as

$$d \epsilon = \text{tr} \left[ cc^\dagger (dH - \epsilon dS) \right] = \text{vec} \left( (cc^\dagger)^\dagger \text{vec}(dH - \epsilon dS) \right)$$

$$= \text{vec}(cc^\dagger)^\dagger [d(\text{vec}H) - \epsilon d(\text{vec}S)]. \quad (2.75)$$

Now, suppose that $a$ is some vector containing nonlinear variational parameters. For generality, we will not specify how many nonlinear parameters there are (i.e. how many components vector $a$ has) and how basis functions depend on them. The gradient of the energy with respect to these parameters is:

$$\nabla_a \epsilon \equiv \frac{\partial \epsilon}{\partial a'} = \text{vec}(cc^\dagger)^\dagger \left( \frac{\partial \text{vec}H}{\partial a'} - \epsilon \frac{\partial \text{vec}S}{\partial a'} \right). \quad (2.76)$$
In practical applications, elements $H_{kl}$ and $S_{kl}$ often depend only on nonlinear parameters of $k$-th and $l$-th basis functions. Thus, the matrix

$$\frac{\partial \operatorname{vec} H}{\partial a'} - \epsilon \frac{\partial \operatorname{vec} S}{\partial a'}$$

is sparse and this fact should be taken into account when expression (2.76) is programmed. This situation takes place when we deal with complex Gaussians. An efficient scheme of computing the entire gradient can be utilized in the following manner. First, we calculate $\nabla \operatorname{vech} L_1 \epsilon$, $\nabla \operatorname{vech} B_1 \epsilon$, $\nabla \operatorname{vech} L_2 \epsilon$, $\ldots$, $\nabla \operatorname{vech} B_k \epsilon$, and then combine them into the total gradient. In turn, the evaluation of $\nabla \operatorname{vech} L_k \epsilon$, as well as $\nabla \operatorname{vech} B_k \epsilon$, can be done using the following expression:

$$\nabla \operatorname{vech} L_k \epsilon \equiv \frac{\partial \epsilon}{\partial \operatorname{vech} L_k}$$

$$= c_k \sum_{l=1}^{K} c_l^* \left[ \frac{\partial H_{lk}}{\partial \operatorname{vech} L_k} - \epsilon \frac{\partial S_{lk}}{\partial \operatorname{vech} L_k} \right] + c_k^* \sum_{l=1}^{K} c_l \left[ \frac{\partial H_{kl}}{\partial \operatorname{vech} L_k} - \epsilon \frac{\partial S_{kl}}{\partial \operatorname{vech} L_k} \right]$$

$$- c_k c_k^* \left[ \frac{\partial H_{kk}}{\partial \operatorname{vech} L_k} - \epsilon \frac{\partial S_{kk}}{\partial \operatorname{vech} L_k} \right]$$

$$= 2 \Re \left( c_k \sum_{l=1}^{K} c_l^* \left[ \frac{\partial H_{lk}}{\partial \operatorname{vech} L_k} - \epsilon \frac{\partial S_{lk}}{\partial \operatorname{vech} L_k} \right] \right) - |c_k|^2 \left[ \frac{\partial H_{kk}}{\partial \operatorname{vech} L_k} - \epsilon \frac{\partial S_{kk}}{\partial \operatorname{vech} L_k} \right].$$

(2.77)

Looking at (2.76) and (2.77) one can see that the calculation of the energy gradient requires the knowledge of the following derivatives:

$$\frac{\partial H_{kl}}{\partial \operatorname{vech} L_k}, \frac{\partial H_{kl}}{\partial \operatorname{vech} L_l}, \frac{\partial H_{kl}}{\partial \operatorname{vech} B_k}, \text{ and } \frac{\partial H_{kl}}{\partial \operatorname{vech} B_l},$$

(2.78)

as well as the corresponding derivatives of $S_{kl}$. We will obtain the formulae for these derivatives below.
2.6.7 Overlap derivatives

Let us begin with the differential for the nonnormalized overlap:

\[
\begin{align*}
\langle \phi_k | \tilde{\phi}_l \rangle &= d \frac{\pi^{3n/2}}{|C_{kl}|^{3/2}} = -\frac{3}{2} \frac{\pi^{3n/2}}{|C_{kl}|^{3/2}} \text{tr} \left[ C_{kl}^{-1} d C_{kl} \right] \\
&= -\frac{3}{2} \langle \phi_k | \tilde{\phi}_l \rangle \text{tr} \left[ C_{kl}^{-1} d(A_k + A_l - iB_k + iB_l) \right] \\
&= -\frac{3}{2} \langle \phi_k | \tilde{\phi}_l \rangle \text{tr} \left[ C_{kl}^{-1} ((d L_k) L_k' + L_k d L_k' + (d \tilde{L}_l) \tilde{L}_l' + \tilde{L}_l d \tilde{L}_l' - i d B_k + i d B_l) \right] \\
&= -\frac{3}{2} \langle \phi_k | \tilde{\phi}_l \rangle \text{tr} \left[ 2 L_k' C_{kl}^{-1} d L_k + 2 \tilde{L}_l' C_{kl}^{-1} d \tilde{L}_l - i C_{kl}^{-1} d B_k + i \tilde{C}_{kl}^{-1} d \tilde{B}_l \right] \\
&= -\frac{3}{2} \langle \phi_k | \tilde{\phi}_l \rangle \text{tr} \left[ 2 L_k' C_{kl}^{-1} d L_k + 2 L_l' P C_{kl}^{-1} P' d L_l - i C_{kl}^{-1} d B_k + i P C_{kl}^{-1} P' d B_l \right].
\end{align*}
\]

(2.79)

To simplify the expression it is convenient to denote

\[
\tilde{C}_{kl} = P \tilde{C}_{kl} P',
\]

(2.80)

so that

\[
P \tilde{C}_{kl}^{-1} P' = (P \tilde{C}_{kl} P')^{-1} = \tilde{C}_{kl}^{-1}.
\]

(2.81)

Using relations (2.11), (2.12), and (2.13) we can transform (2.79) in the following manner:

\[
\begin{align*}
d \langle \phi_k | \tilde{\phi}_l \rangle &= -\frac{3}{2} \langle \phi_k | \tilde{\phi}_l \rangle \left[ 2 \text{vec}(C_{kl}^{-1} L_k) \text{vec}(d L_k) + 2 \text{vec}(\tilde{C}_{kl}^{-1} L_l) \text{vec}(d L_l) \\
&- i \text{vec}(\tilde{C}_{kl}^{-1}) \text{vec}(d B_k) + i \text{vec}(\tilde{C}_{kl}^{-1}) \text{vec}(d B_l) \right] \\
&= -\frac{3}{2} \langle \phi_k | \tilde{\phi}_l \rangle \left[ 2 \text{vech}(C_{kl}^{-1} L_k) \text{d vech} L_k + 2 \text{vech}(\tilde{C}_{kl}^{-1} L_l) \text{d vech} L_l \\
&- i \text{vech}(2 \tilde{C}_{kl}^{-1} - \text{diag} \tilde{C}_{kl}^{-1}) \text{d vech} B_k + i \text{vech}(2 \tilde{C}_{kl}^{-1} - \text{diag} \tilde{C}_{kl}^{-1}) \text{d vech} B_l \right].
\end{align*}
\]

(2.82)
It follows from the last formula that:

\[
\frac{\partial \langle \tilde{\phi}_k | \tilde{\phi}_l \rangle}{\partial (\text{vech } L_k)'} = -3 \langle \phi_k | \tilde{\phi}_l \rangle \text{ vech}(\tilde{C}^{-1}_{kl}L_k)', \tag{2.83}
\]

\[
\frac{\partial \langle \phi_k | \tilde{\phi}_l \rangle}{\partial (\text{vech } L_l)'} = -3 \langle \phi_k | \tilde{\phi}_l \rangle \text{ vech}(\tilde{C}^{-1}_{kl}L_l)', \tag{2.84}
\]

\[
\frac{\partial \langle \phi_k | \tilde{\phi}_l \rangle}{\partial (\text{vech } B_k)'} = \frac{3}{2} i \langle \phi_k | \tilde{\phi}_l \rangle \text{ vech}(2\tilde{C}^{-1}_{kl} - \text{diag } \tilde{C}^{-1}_{kl})', \tag{2.85}
\]

\[
\frac{\partial \langle \phi_k | \tilde{\phi}_l \rangle}{\partial (\text{vech } B_l)'} = -\frac{3}{2} i \langle \phi_k | \tilde{\phi}_l \rangle \text{ vech}(2\tilde{C}^{-1}_{kl} - \text{diag } \tilde{C}^{-1}_{kl})'. \tag{2.86}
\]

For the case when \( k = l \) and \( \hat{P} = 1 \) we obtain:

\[
\frac{\partial \langle \phi_k | \phi_k \rangle}{\partial (\text{vech } L_k)'} = -6 \langle \phi_k | \phi_k \rangle \text{ vech}(C^{-1}_{kk}L_k)',
\]

\[
= -3 \langle \phi_k | \phi_k \rangle \text{ vech}(A^{-1}_kL_k)' = -3 \langle \phi_k | \phi_k \rangle \text{ vech}((L^{-1}_k)')', \tag{2.87}
\]

and

\[
\frac{\partial \langle \phi_k | \phi_k \rangle}{\partial (\text{vech } B_k)'} = 0. \tag{2.88}
\]

Knowing the derivatives of the nonnormalized overlap matrix elements it is now straightforward to obtain the corresponding expressions for the normalized overlap, \( S_{kl} \):

\[
\frac{\partial S_{kl}}{\partial (\text{vech } L_k)'} = \frac{\partial}{\partial (\text{vech } L_k)'} \frac{\langle \phi_k | \tilde{\phi}_l \rangle}{\sqrt{\langle \phi_k | \phi_k \rangle \langle \tilde{\phi}_l | \tilde{\phi}_l \rangle}} \frac{\partial \langle \phi_k | \tilde{\phi}_l \rangle}{\partial (\text{vech } L_k)'}
\]

\[
= \frac{1}{\sqrt{\langle \phi_k | \phi_k \rangle \langle \tilde{\phi}_l | \tilde{\phi}_l \rangle}} \frac{\partial \langle \phi_k | \tilde{\phi}_l \rangle}{\partial (\text{vech } L_k)'} - \frac{1}{2} \frac{\langle \phi_k | \tilde{\phi}_l \rangle}{\sqrt{\langle \phi_k | \phi_k \rangle \langle \tilde{\phi}_l | \tilde{\phi}_l \rangle}} \frac{\partial \langle \phi_k | \phi_k \rangle}{\partial (\text{vech } L_k)'} \frac{1}{\langle \phi_k | \phi_k \rangle} \frac{\partial \langle \phi_k | \phi_k \rangle}{\partial (\text{vech } L_k)'}
\]

\[
= S_{kl} \left[ -3 \text{ vech}(\tilde{C}^{-1}_{kl}L_k)' - \frac{1}{2} (-3) \text{ vech}((L^{-1}_k)')' \right]
\]

\[
= \frac{3}{2} S_{kl} \text{ vech}\left((L^{-1}_k)' - 2\tilde{C}^{-1}_{kl}L_k)'\right). \tag{2.89}
\]
Other derivatives of the normalized overlap are:

\[
\frac{\partial S_{kl}}{\partial (\text{vech} \ L_l)} = \frac{3}{2} S_{kl} \text{vech} \left((L_l^{-1})' - 2\tilde{C}_{kl}^{-1}L_l\right)',
\]

(2.90)

\[
\frac{\partial S_{kl}}{\partial (\text{vech} \ B_k)} = \frac{1}{\sqrt{\langle \phi_k|\phi_k\rangle \langle \phi_l|\phi_l\rangle}} \frac{\partial \langle \phi_k|\tilde{\phi}_l\rangle}{\partial (\text{vech} \ B_k)'} = \frac{3}{2} i S_{kl} \text{vech} \left(2\tilde{C}_{kl}^{-1} - \text{diag} \tilde{C}_{kl}^{-1}\right)',
\]

(2.91)

\[
\frac{\partial S_{kl}}{\partial (\text{vech} \ B_l)} = -\frac{3}{2} i S_{kl} \text{vech} \left(2\tilde{C}_{kl}^{-1} - \text{diag} \tilde{C}_{kl}^{-1}\right)'.
\]

(2.92)

2.6.8 Kinetic energy derivatives

Taking the differential of the expression for the normalized kinetic energy matrix element (2.46) gives the following:

\[
dT_{kl} = d \left(6 S_{kl} \text{tr} \left[M \tilde{C}_{kl} \tilde{C}_{kl}^{-1} C_k^\dagger \right]\right)
= 6 \text{tr} \left[M \tilde{C}_{kl} \tilde{C}_{kl}^{-1} C_k^\dagger \right] dS_{kl} + 6S_{kl} \text{tr} \left[M d(\tilde{C}_{kl} \tilde{C}_{kl}^{-1} C_k^\dagger)\right].
\]

(2.93)

Using the fact that for an arbitrary square matrix \(X\),

\[
d(X^{-1}) = -X^{-1}(dX)X^{-1}
\]

(2.94)

the differential in the last term of (2.93) can be expanded as

\[
d(\tilde{C}_{kl} \tilde{C}_{kl}^{-1} C_k^\dagger)
= d(\tilde{C}_{kl}) \tilde{C}_{kl}^{-1} C_k^\dagger + \tilde{C}_{kl}(d \tilde{C}_{kl}^{-1}) C_k^\dagger + \tilde{C}_{kl} \tilde{C}_{kl}^{-1} d C_k^\dagger
= d(\tilde{C}_{kl}) \tilde{C}_{kl}^{-1} C_k^\dagger - \tilde{C}_{kl} \tilde{C}_{kl}^{-1} (d \tilde{C}_{kl}) \tilde{C}_{kl}^{-1} C_k^\dagger + \tilde{C}_{kl} \tilde{C}_{kl}^{-1} d C_k^\dagger
= d(\tilde{C}_{kl}) \tilde{C}_{kl}^{-1} C_k^\dagger - \tilde{C}_{kl} \tilde{C}_{kl}^{-1} (d C_k) \tilde{C}_{kl}^{-1} C_k^\dagger - \tilde{C}_{kl} \tilde{C}_{kl}^{-1} (d \tilde{C}_{kl}) \tilde{C}_{kl}^{-1} C_k^\dagger + \tilde{C}_{kl} \tilde{C}_{kl}^{-1} d C_k^\dagger.
\]

(2.95)
Expression (2.93) then becomes:

\[
d_T_{kl} = \frac{T_{kl}}{S_{kl}} \, d\, S_{kl} + 6S_{kl} \, \text{tr} \left[ MC_k^\dagger \tilde{C}_k^{-1} \, d\, \tilde{C}_I - \tilde{C}_{kl}^{-1} C_k^\dagger M \tilde{C}_I \tilde{C}_k^{-1} \, d\, \tilde{C}_I \right] \\
+ M \tilde{C}_I \tilde{C}_k^{-1} \, d\, C_k^\dagger - \tilde{C}_{kl}^{-1} C_k^\dagger M \tilde{C}_I \tilde{C}_k^{-1} \, d\, C_k^\dagger \\
= \frac{T_{kl}}{S_{kl}} \, d\, S_{kl} + 6S_{kl} \, \text{tr} \left[ \tilde{C}_{kl}^{-1} C_k^\dagger M \, d\, \tilde{C}_I - \tilde{C}_{kl}^{-1} C_k^\dagger M \tilde{C}_I \tilde{C}_k^{-1} \, d\, \tilde{C}_I \right] \\
+ \tilde{C}_{kl}^{-1} \tilde{C}_I M \, d\, C_k^\dagger - \tilde{C}_{kl}^{-1} \tilde{C}_I M \tilde{C}_k C_k^{-1} \, d\, C_k^\dagger \\
= \frac{T_{kl}}{S_{kl}} \, d\, S_{kl} + 6S_{kl} \, \text{tr} \left[ \tilde{C}_{kl}^{-1} C_k^\dagger M \tilde{C}_I \tilde{C}_k^{-1} \, d\, \tilde{C}_I + \tilde{C}_{kl}^{-1} \tilde{C}_I M \tilde{C}_I \tilde{C}_k^{-1} \, d\, C_k^\dagger \right]. \quad (2.96)
\]

Next, we plug

\[
d\, \tilde{C}_I = (d\, \tilde{L}_I) \tilde{L}_I + \tilde{L}_I \, d\, \tilde{L}_I + i \, d\, \tilde{B}_I, \quad (2.97)
\]

\[
d\, C_k^\dagger = (d\, L_k) L_k' + L_k \, d\, L_k' - i \, d\, B_k, \quad (2.98)
\]

into (2.96) and obtain:

\[
d_T_{kl} = \frac{T_{kl}}{S_{kl}} \, d\, S_{kl} + 6S_{kl} \, \text{tr} \left[ 2L_k' \tilde{C}_{kl}^{-1} \tilde{C}_I M \tilde{C}_I \tilde{C}_k^{-1} \, d\, L_k + 2\tilde{L}_I' \tilde{C}_{kl}^{-1} C_k^\dagger M C_k^\dagger \tilde{C}_k^{-1} \, d\, \tilde{L}_I \\
- i\tilde{C}_{kl}^{-1} \tilde{C}_I M \tilde{C}_k \tilde{C}_k^{-1} \, d\, B_k + i\tilde{C}_{kl}^{-1} C_k^\dagger M C_k^\dagger \tilde{C}_k^{-1} \, d\, \tilde{B}_I \right]. \quad (2.99)
\]

In order to make the formulae more compact let us introduce the following notations:

\[
F = \tilde{C}_{kl}^{-1} \tilde{C}_I M \tilde{C}_I \tilde{C}_k^{-1}, \quad (2.100)
\]

\[
G = P\tilde{C}_{kl}^{-1} C_k^\dagger M C_k^\dagger \tilde{C}_k^{-1} P'. \quad (2.101)
\]

With this we have:

\[
d_T_{kl} = \frac{T_{kl}}{S_{kl}} \, d\, S_{kl} + 6S_{kl} \, \text{tr} \left[ 2L_k' F \, d\, L_k + 2\tilde{L}_I' G \, d\, \tilde{L}_I - iF \, d\, B_k + iG \, d\, \tilde{B}_I \right], \quad (2.102)
\]
which then can be transformed as follows:

\[
\begin{align*}
d T_{kl} &= \frac{T_{kl}}{S_{kl}} \, d S_{kl} + 6 S_{kl} \left[ 2 \, \text{vec}(F L_k)' \, \text{vec}(d L_k) \\
&\quad + 2 \, \text{vec}(G L_l)' \, \text{vec}(d L_l) - i \, \text{vec}(F)' \, \text{vec}(d B_k) + i \, \text{vec}(G)' \, \text{vec}(d B_l) \right] \\
&= \frac{T_{kl}}{S_{kl}} \, d S_{kl} + 6 S_{kl} \left[ 2 \, \text{vech}(F L_k)' \, \text{vech}(L_k) + 2 \, \text{vech}(G L_l)' \, \text{vech}(L_l) \\
&\quad - i \, \text{vech}(2F - \text{diag}(F))' \, \text{vech}(B_k) + i \, \text{vech}(2G - \text{diag}(G))' \, \text{vech}(B_l) \right].
\end{align*}
\]

(2.103)

Thus, we can see that the derivatives of the normalized kinetic energy matrix element are:

\[
\begin{align*}
\frac{\partial T_{kl}}{\partial (\text{vech } L_k)'} &= \frac{T_{kl}}{S_{kl}} \, \frac{\partial S_{kl}}{\partial (\text{vech } L_k)'} + 12 S_{kl} \, \text{vech}(F L_k)', \\
&\quad (2.104) \\
\frac{\partial T_{kl}}{\partial (\text{vech } L_l)'} &= \frac{T_{kl}}{S_{kl}} \, \frac{\partial S_{kl}}{\partial (\text{vech } L_l)'} + 12 S_{kl} \, \text{vech}(G L_l)', \\
&\quad (2.105) \\
\frac{\partial T_{kl}}{\partial (\text{vech } B_k)'} &= \frac{T_{kl}}{S_{kl}} \, \frac{\partial S_{kl}}{\partial (\text{vech } B_k)'} - 6i S_{kl} \, \text{vech}(2F - \text{diag}(F))', \\
&\quad (2.106) \\
\frac{\partial T_{kl}}{\partial (\text{vech } B_l)'} &= \frac{T_{kl}}{S_{kl}} \, \frac{\partial S_{kl}}{\partial (\text{vech } B_l)'} + 6i S_{kl} \, \text{vech}(2G - \text{diag}(G))'. \\
&\quad (2.107)
\end{align*}
\]

2.6.9 Potential energy derivatives

To write out the expression for the derivatives of the potential energy matrix element \((2.64)\) with respect to nonlinear variational parameters we first need to evaluate the corresponding expressions for \(R_{kl}^{ij}\). We start with taking the differential of \((2.63)\):

\[
\begin{align*}
d R_{kl}^{ij} &= \frac{R_{kl}^{ij}}{S_{kl}} \, d S_{kl} + \frac{2}{\sqrt{\pi}} S_{kl} \, d \text{tr} \left[ \tilde{C}_{kl}^{-1} J_{ij} \right]^{-1/2} \\
&= \frac{R_{kl}^{ij}}{S_{kl}} \, d S_{kl} - \frac{1}{\sqrt{\pi}} S_{kl} \, \text{tr} \left[ \tilde{C}_{kl}^{-1} J_{ij} \right]^{-3/2} \text{tr} \left[ (d \tilde{C}_{kl}^{-1}) J_{ij} \right] \\
&= \frac{R_{kl}^{ij}}{S_{kl}} \, d S_{kl} + \frac{1}{\sqrt{\pi}} S_{kl} \, \text{tr} \left[ \tilde{C}_{kl}^{-1} J_{ij} \right]^{-3/2} \text{tr} \left[ \tilde{C}_{kl}^{-1} (d \tilde{C}_{kl}) \tilde{C}_{kl}^{-1} J_{ij} \right].
\end{align*}
\]

(2.108)
After inserting (2.98) and (2.97) we transform it as follows:

\[
\begin{align*}
\text{d} R_{kl}^{ij} &= \frac{R_{kl}^{ij}}{S_{kl}} \text{d} S_{kl} + \frac{1}{\sqrt{\pi}} S_{kl} \text{tr} \left[ \tilde{C}^{-1}_{kl} J_{ij} \right]^{-3/2} \text{tr} \left[ \tilde{C}^{-1}_{kl} J_{ij} \tilde{C}^{-1}_{kl} \left( \text{d} L_k \right) L_k' \right] \nonumber \\
&+ L_k \text{d} L_k' + \left( \text{d} \tilde{L}_l \right) \tilde{L}_l' + \tilde{L}_l \text{d} \tilde{L}_l' - i \text{d} B_k + i \text{d} \tilde{B}_l \right] \\
&= \frac{R_{kl}^{ij}}{S_{kl}} \text{d} S_{kl} + \frac{1}{\sqrt{\pi}} S_{kl} \text{tr} \left[ \tilde{C}^{-1}_{kl} J_{ij} \right]^{-3/2} \text{tr} \left[ 2 L_k' \tilde{C}^{-1}_{kl} J_{ij} \tilde{C}^{-1}_{kl} \text{d} L_k \right] \\
&+ 2 L_l' P \tilde{C}^{-1}_{kl} J_{ij} \tilde{C}^{-1}_{kl} P' \text{d} L_l - i \tilde{C}^{-1}_{kl} J_{ij} \tilde{C}^{-1}_{kl} \text{d} B_k + i P \tilde{C}^{-1}_{kl} J_{ij} \tilde{C}^{-1}_{kl} \text{d} B_l \right]. \\
\end{align*}
\]

(2.109)

If we denote

\[
\tilde{Q} = \tilde{C}^{-1}_{kl} J_{ij} \tilde{C}^{-1}_{kl}, \\
\tilde{\tilde{Q}} = P \tilde{Q} P',
\]

(2.110) (2.111)

then

\[
\begin{align*}
\text{d} R_{kl}^{ij} &= \frac{R_{kl}^{ij}}{S_{kl}} \text{d} S_{kl} + \frac{1}{\sqrt{\pi}} S_{kl} \text{tr} \left[ \tilde{C}^{-1}_{kl} J_{ij} \right]^{-3/2} \left[ 2 \text{vec}(\tilde{Q} L_k)' \text{vec}(\text{d} L_k) \right. \\
&+ 2 \text{vec}(\tilde{Q} L_l)' \text{vec}(\text{d} L_l) - i \text{vec}(\tilde{Q})' \text{vec}(\text{d} B_k) + i \text{vec}(\tilde{Q})' \text{vec}(\text{d} B_l) \left. \right] \\
&= \frac{R_{kl}^{ij}}{S_{kl}} \text{d} S_{kl} + \frac{1}{\sqrt{\pi}} S_{kl} \text{tr} \left[ \tilde{C}^{-1}_{kl} J_{ij} \right]^{-3/2} \\
&\times \left[ 2 \text{vech}(\tilde{Q} L_k)' \text{d} \text{vech} L_k + 2 \text{vech}(\tilde{Q} L_l)' \text{d} \text{vech} L_l \right. \\
&- i \text{vech}(2\tilde{Q} - \text{diag}(\tilde{Q}))' \text{vech}(\text{d} B_k) + i \text{vech}(2\tilde{Q} - \text{diag}(\tilde{Q}))' \text{vech}(\text{d} B_l) \left. \right] \\
\end{align*}
\]

(2.112)
Hence, the derivatives of $R_{kl}^{ij}$ $(k \neq l)$ are:

\[
\frac{\partial R_{kl}^{ij}}{\partial (\text{vech } L_k)^y} = \frac{R_{kl}^{ij}}{S_{kl}} \frac{\partial S_{kl}}{\partial (\text{vech } L_k)^y} + \frac{2}{\sqrt{\pi}} S_{kl} \text{ tr } \left[ \tilde{C}_{kl}^{-1} J_{ij} \right]^{-3/2} \text{vech}(\tilde{Q} L_k)',
\] (2.113)

\[
\frac{\partial R_{kl}^{ij}}{\partial (\text{vech } L_l)^y} = \frac{R_{kl}^{ij}}{S_{kl}} \frac{\partial S_{kl}}{\partial (\text{vech } L_l)^y} + \frac{2}{\sqrt{\pi}} S_{kl} \text{ tr } \left[ \tilde{C}_{kl}^{-1} J_{ij} \right]^{-3/2} \text{vech}(\tilde{Q} L_l)',
\] (2.114)

\[
\frac{\partial R_{kl}^{ij}}{\partial (\text{vech } B_k)^y} = \frac{R_{kl}^{ij}}{S_{kl}} \frac{\partial S_{kl}}{\partial (\text{vech } B_k)^y} - \frac{i}{\sqrt{\pi}} S_{kl} \text{ tr } \left[ \tilde{C}_{kl}^{-1} J_{ij} \right]^{-3/2} \text{vech}(2\tilde{Q} - \text{diag}(\tilde{Q}))',
\] (2.115)

\[
\frac{\partial R_{kl}^{ij}}{\partial (\text{vech } B_l)^y} = \frac{R_{kl}^{ij}}{S_{kl}} \frac{\partial S_{kl}}{\partial (\text{vech } B_l)^y} + \frac{i}{\sqrt{\pi}} S_{kl} \text{ tr } \left[ \tilde{C}_{kl}^{-1} J_{ij} \right]^{-3/2} \text{vech}(2\tilde{Q} - \text{diag}(\tilde{Q}))'.
\] (2.116)

The derivatives of the potential energy matrix element (2.64) are nothing but linear combinations of (2.113)–(2.116):

\[
\frac{\partial V_{kl}}{\partial (\text{vech } L_k)^y} = \sum_{i=1}^{n} q_i q_j \frac{\partial R_{kl}^{ij}}{\partial (\text{vech } L_k)^y} + \sum_{i<j}^{n} q_i q_j \frac{\partial R_{kl}^{ij}}{\partial (\text{vech } L_k)^y} \\
= \frac{V_{kl}}{S_{kl}} \frac{\partial S_{kl}}{\partial (\text{vech } L_k)^y} + \frac{2}{\sqrt{\pi}} S_{kl} \left( \sum_{i=1}^{n} q_i q_j \text{ tr } \left[ \tilde{C}_{kl}^{-1} J_{ij} \right]^{-3/2} \text{vech}(\tilde{Q} L_k)' \right) + \\
+ \sum_{i<j}^{n} q_i q_j \text{ tr } \left[ \tilde{C}_{kl}^{-1} J_{ij} \right]^{-3/2} \text{vech}(\tilde{Q} L_k)',
\] (2.117)

\[
\frac{\partial V_{kl}}{\partial (\text{vech } L_l)^y} = \frac{V_{kl}}{S_{kl}} \frac{\partial S_{kl}}{\partial (\text{vech } L_l)^y} + \frac{2}{\sqrt{\pi}} S_{kl} \left( \sum_{i=1}^{n} q_i q_j \text{ tr } \left[ \tilde{C}_{kl}^{-1} J_{ij} \right]^{-3/2} \text{vech}(\tilde{Q} L_l)' \right) + \\
+ \sum_{i<j}^{n} q_i q_j \text{ tr } \left[ \tilde{C}_{kl}^{-1} J_{ij} \right]^{-3/2} \text{vech}(\tilde{Q} L_l)',
\] (2.118)

\[
\frac{\partial V_{kl}}{\partial (\text{vech } B_k)^y} = \frac{V_{kl}}{S_{kl}} \frac{\partial S_{kl}}{\partial (\text{vech } B_k)^y} \\
- \frac{i}{\sqrt{\pi}} S_{kl} \left( \sum_{i=1}^{n} q_i q_j \text{ tr } \left[ \tilde{C}_{kl}^{-1} J_{ij} \right]^{-3/2} \text{vech}(2\tilde{Q} - \text{diag}(\tilde{Q}))' \right) + \\
+ \sum_{i<j}^{n} q_i q_j \text{ tr } \left[ \tilde{C}_{kl}^{-1} J_{ij} \right]^{-3/2} \text{vech}(2\tilde{Q} - \text{diag}(\tilde{Q}))',
\] (2.119)
\[
\frac{\partial V_{kl}}{\partial(\text{vech } B_l)'} = V_{kl} \frac{\partial S_{kl}}{S_{kl} \partial(\text{vech } B_l)'} \\
+ \frac{i}{\sqrt{\pi}} S_{kl} \left( \sum_{i=1}^{n} q_i q_i \text{tr} \left[ \tilde{C}_{kl}^{-1} J_{ii} \right]^{-3/2} \text{vech}(2\tilde{Q} - \text{diag}(\tilde{Q}))' \\
+ \sum_{i<j} q_i q_j \text{tr} \left[ \tilde{C}_{kl}^{-1} J_{ij} \right]^{-3/2} \text{vech}(2\tilde{Q} - \text{diag}(2\tilde{Q}))' \right). 
\]

(2.120)

One final comment we would like to make regarding the evaluation of the potential energy derivatives is that there are many products \( \tilde{C}_{kl}^{-1} J_{ij} \tilde{C}_{kl}^{-1} \) appear in the expressions above. For an arbitrary matrix \( X \) the elements of these products can be easily computed using the following relations:

\[
(XJ_{ii}X)_{pq} = (X)_{pi}(X)_{iq}, \\
(XJ_{ij}X)_{pq} = (X)_{pi}(X)_{iq} + (X)_{pj}(X)_{jq} \\
- (X)_{pi}(X)_{jq} \quad i \neq j. 
\]

(2.121)

### 2.7 Matrix elements with Gaussians containing premultipliers

In this section we present matrix elements with Gaussian basis functions containing premultipliers in the form of even powers of \( r_1 \):

\[
\varphi_k = r_1^{m_k} \exp \left[ -r'A_k r \right]. 
\]

(2.122)

We will use symbol \( \varphi \) to denote them, while real one-center Gaussians without premultipliers will be denoted by means of \( \phi \):

\[
\phi_k = \exp \left[ -r'A_k r \right]. 
\]

(2.123)

These are a partial case of the former ones and will refer to some of the expressions for Gaussians without premultipliers obtained before.

For the sake of simplicity, we will be working with matrix elements that do not have any permutational operators in them. In the case when the exponential parameters are real, the inclusion of such operators is fairly straightforward. One
just needs to transform matrix $A_k$ of the ket accordingly. Our derivations below are based on the content of papers [6] and [24], but here they are presented in a more detailed way.

2.7.1 Overlap

The overlap of functions (2.122) can be easily obtained using general formula (2.61). In this case we put $\nu = m_k + m_l$. The result for nonnormalized basis functions is

$$\langle \varphi_k | \varphi_l \rangle = \langle \phi_k | r_1^{m_k+1} \phi_l \rangle = \frac{2}{\sqrt{\pi}} \Gamma \left( \frac{m_{kl} + 3}{2} \right) (A_{kl}^{-1})_{11}^{m_{kl}/2} \langle \phi_k | \phi_l \rangle.$$  \hspace{1cm} (2.124)

Here we introduced the notation $m_{kl} \equiv m_k + m_l$, which will be used in many expressions below.

The overlap with normalized basis functions, after simplification, takes the following form:

$$S_{kl} = \frac{\langle \varphi_k | \varphi_l \rangle}{\langle \varphi_k | \varphi_k \rangle \langle \varphi_l | \varphi_l \rangle}^{1/2} = \gamma_1(m_k, m_l) 2^{3/2} \left( \frac{(A_{kl}^{-1})_{11}}{(A_{k}^{-1})_{11}} \right)^{m_k} \left( \frac{(A_{kl}^{-1})_{11}}{(A_{l}^{-1})_{11}} \right)^{m_l} \left( \frac{||L_k|| \cdot ||L_k||}{|A_{kl}|} \right)^{3/2},$$ \hspace{1cm} (2.125)

where $||L_k||$ denotes the absolute value of the determinant of the Cholesky factor of $A_k$, and

$$\gamma_1(m_k, m_l) = 2^{-m_{kl}} \frac{\Gamma \left( \frac{m_{kl}+3}{2} \right)}{\left[ \Gamma \left( m_k + \frac{3}{2} \right) \Gamma \left( m_l + \frac{3}{2} \right) \right]^{1/2}}$$ \hspace{1cm} (2.126)

is a constant that depends on $m_k$ and $m_l$. This constant, as well as two other constants that we will define a later, can be precomputed for a range of $m_k$ and $m_l$ values to speed up matrix element calculations.

2.7.2 Kinetic energy

To evaluate the integral

$$\langle \varphi_k | -\nabla_r M \nabla_r | \varphi_l \rangle = \langle \nabla' r_1^{m_k} \phi_k | M | \nabla r_1^{m_l} \phi_l \rangle,$$ \hspace{1cm} (2.127)
w preliminary results will be needed. First we want to note that \( r_1^{mk} \) in (2.122) can be conveniently written as the square root of quadratic form in \( r \) using the matrix \( J_{11} \):

\[
  r_1^{mk} = [r' J_{11} r]^{mk/2}.
\]  

(2.128)

With this we can evaluate the gradient of \( \varphi_k \) with respect to vector \( r \):

\[
  \nabla_r \varphi_k = -2 \phi_k A_k r,
\]

\[
  \nabla_r \varphi_k = \nabla_r [r' J_{11} r]^{mk/2} \phi_k = [r' J_{11} r]^{mk/2} \phi_k \left( \frac{m_k}{r_1^2} J_{11} r - 2A_k r \right).
\]

Hence,

\[
  \langle \varphi_k | -\nabla_r^t M \nabla_r | \varphi_l \rangle
  = \left\langle \phi_k \left| [r' J_{11} r]^{mk/2} \left( \frac{m_k}{r_1^2} J_{11} r - 2A_k r \right) M [r' J_{11} r]^{ml/2} \left( \frac{m_l}{r_1^2} J_{11} r - 2A_l r \right) \right| \phi_l \right\rangle
  = \left\langle \phi_k \left| [r' J_{11} r]^{mk/2} \frac{m_k m_l}{r_1^2} r' J_{11} M J_{11} r \right| \phi_l \right\rangle - 2 \left\langle \phi_k \left| [r' J_{11} r]^{mk/2} \frac{m_k}{r_1^2} r' J_{11} M A_l r \right| \phi_l \right\rangle
  - 2 \left\langle \phi_k \left| [r' J_{11} r]^{mk/2} \frac{m_l}{r_1^2} r' A_k M J_{11} r \right| \phi_l \right\rangle + 4 \left\langle \phi_k \left| [r' J_{11} r]^{mk/2} r' A_k M A_l r \right| \phi_l \right\rangle.
\]

(2.129)

Making use of the fact that for an arbitrary matrix \( X \),

\[
  r' X r = tr[X r r'] = (\text{vec} X')' \text{vec}(r r'),
\]

and replacing \( r' J_{11} M J_{11} r \) with \( r_1^2 M_{11} \), we now have:
\[
\langle \varphi_k | -\nabla'_r M \nabla_r | \varphi_l \rangle \\
= m_k m_l M_{11} \left\langle \varphi_k \left| \frac{1}{r_1^2} \right| \varphi_l \right\rangle - 2m_k (\text{vec}(A_l M J_{11}))' \left\langle \varphi_k \left| \frac{\text{vec}(r')} {r_1^2} \right| \varphi_l \right\rangle \\
- 2m_l (\text{vec}(J_{11} M A_k))' \left\langle \varphi_k \left| \frac{\text{vec}(r')} {r_1^2} \right| \varphi_l \right\rangle + 4(\text{vec}(A_l M A_k))' \left\langle \varphi_k | \text{vec}(r') | \varphi_l \right\rangle \\
= m_k m_l M_{11} \left\langle \varphi_k \left| \frac{1}{r_1^2} \right| \varphi_l \right\rangle + 2m_k (\text{vec}(A_l M J_{11}))' \frac{\partial}{\partial \text{vec} A_{kl}} \left\langle \varphi_k \left| \frac{1}{r_1^2} \right| \varphi_l \right\rangle \\
+ 2m_l (\text{vec}(J_{11} M A_k))' \frac{\partial}{\partial \text{vec} A_{kl}} \left\langle \varphi_k \left| \frac{1}{r_1^2} \right| \varphi_l \right\rangle - 4(\text{vec}(A_l M A_k))' \frac{\partial}{\partial \text{vec} A_{kl}} \langle \varphi_k | \varphi_l \rangle \\
(2.130)
\]

In the last formula we used the relation
\[
\langle \varphi_k | \text{vec}(r') | \varphi_l \rangle = -\frac{\partial}{\partial \text{vec} A_{kl}} \langle \varphi_k | \varphi_l \rangle.
\]

The gradient of the overlap with respect to \((\text{vec} A_{kl})')'\) is
\[
\frac{\partial}{\partial (\text{vec} A_{kl})'} \langle \varphi_k | \varphi_l \rangle = 2\pi^{2n-1} \Gamma \left( \frac{m_{kl} + 3}{2} \right) \\
\times \left\{ \text{tr}[A^{-1}_{kl} J_{11}]^{m_{kl}/2} \frac{\partial}{\partial (\text{vec} A_{kl})'} \left| A_{kl} \right|^{3/2} + \frac{1}{|A_{kl}|^{3/2}} \frac{\partial}{\partial (\text{vec} A_{kl})'} \text{tr}[A^{-1}_{kl} J_{11}]^{m_{kl}/2} \right\} \\
(2.131)
\]

It is known from matrix differential calculus that for a matrix variable \(X\) and a constant matrix \(C\) the following is true:
\[
d|X| = |X| \text{tr}[X^{-1} dX] = |X| (\text{vec}(X^{-1}'))' d \text{vec}(X),
\]
\[
\frac{\partial |X|}{\partial (\text{vec} X)'} = |X| (\text{vec}(X^{-1}'))',
\]
and
\[
d \text{tr}[C X^{-1}] = (\text{vec} C')' \text{vec}(X^{-1}) = (\text{vec} C')' [- (X')^{-1} \otimes X^{-1}] d \text{vec} X,
\]
\[
\frac{\partial \text{tr}[C X^{-1}]}{\partial \text{vec}(X)'} = -(\text{vec} C')' [(X')^{-1} \otimes X^{-1}].
\]
Applying these differentiation rules to the expression (2.131) one obtains
\[
\frac{\partial}{\partial (\text{vec } A_{kl})'} \langle \varphi_k | \varphi_l \rangle
= \langle \varphi_k | \varphi_l \rangle \left\{ -\frac{3}{2} \text{vec}(A^{-1}_{kl})' - \frac{m_{kl}}{2} \frac{1}{\text{tr} [A_{kl}^{-1} J_{11}]} (\text{vec } J_{11})' \left[ A_{kl}^{-1} \otimes A_{kl}^{-1} \right] \right\} \tag{2.132}
\]
or
\[
\frac{\partial}{\partial \text{vec } A_{kl}} \langle \varphi_k | \varphi_l \rangle
= \langle \varphi_k | \varphi_l \rangle \left\{ -\frac{3}{2} \text{vec}(A^{-1}_{kl}) - \frac{m_{kl}}{2} \frac{1}{(A_{kl}^{-1})_{11}} \left[ A_{kl}^{-1} \otimes A_{kl}^{-1} \right] \text{vec } J_{11} \right\}. \tag{2.133}
\]

Hence, the matrix elements appearing in the kinetic energy are:
\[
\langle \varphi_k | \frac{1}{r_1^2} | \varphi_l \rangle = \frac{2}{m_{kl} + 1} \frac{1}{(A_{kl}^{-1})_{11}} \langle \varphi_k | \varphi_l \rangle, \tag{2.134}
\]
\[
\frac{\partial}{\partial \text{vec } A_{kl}} \langle \varphi_k | \varphi_l \rangle
= \left\{ -\frac{3}{2} \text{vec}(A_{kl}^{-1}) - \frac{m_{kl}}{2} \frac{1}{(A_{kl}^{-1})_{11}} \text{vec}(A_{kl}^{-1} J_{11} A_{kl}^{-1}) \right\} \langle \varphi_k | \varphi_l \rangle, \tag{2.135}
\]
\[
\frac{\partial}{\partial \text{vec } A_{kl}} \langle \varphi_k | \frac{1}{r_1^2} | \varphi_l \rangle
= \left\{ -\frac{3}{2} \text{vec}(A_{kl}^{-1}) - \frac{m_{kl}}{2} \frac{1}{(A_{kl}^{-1})_{11}} \text{vec}(A_{kl}^{-1} J_{11} A_{kl}^{-1}) \right\} \frac{2}{m_{kl} + 1} \frac{1}{(A_{kl}^{-1})_{11}}, \tag{2.136}
\]
where we used the fact that \([X' \otimes Y] \text{vec}(Z) = \text{vec}(YZX)\). The kinetic energy matrix element is then
\[
\langle \varphi_k | -\nabla'_r M \nabla_r | \varphi_l \rangle
= m_k m_l M_{11} \frac{2}{m_{kl} + 1} \frac{1}{(A_{kl}^{-1})_{11}} \langle \varphi_k | \varphi_l \rangle
- m_k (\text{vec}(A_l J_{11}))' \left\{ 3 \text{vec}(A_{kl}^{-1}) + \frac{m_{kl} - 2}{(A_{kl}^{-1})_{11}} \text{vec}(A_{kl}^{-1} J_{11} A_{kl}^{-1}) \right\} \frac{2}{m_{kl} + 1} \frac{1}{(A_{kl}^{-1})_{11}} \langle \varphi_k | \varphi_l \rangle
- m_l (\text{vec}(J_{11} M A_k))' \left\{ 3 \text{vec}(A_{kl}^{-1}) + \frac{m_{kl} - 2}{(A_{kl}^{-1})_{11}} \text{vec}(A_{kl}^{-1} J_{11} A_{kl}^{-1}) \right\} \frac{2}{m_{kl} + 1} \frac{1}{(A_{kl}^{-1})_{11}} \langle \varphi_k | \varphi_l \rangle
+ 2(\text{vec}(A_l M A_k))' \left\{ 3 \text{vec}(A_{kl}^{-1}) + \frac{m_{kl}}{(A_{kl}^{-1})_{11}} \text{vec}(A_{kl}^{-1} J_{11} A_{kl}^{-1}) \right\} \langle \varphi_k | \varphi_l \rangle. \tag{2.137}
\]
After simplification and rearrangement the final expression for the kinetic energy takes the following form:

\[
T_{kl} = 6 \text{tr}[A_k M A_l A_{kl}^{-1}] S_{kl}
\]

\[
+ \frac{2}{(A_{kl}^{-1})_{11}} \left[ m_k m_l M_{11} \frac{A_{kl}^{-1} A_k M A_l A_{kl}^{-1}}{m_{kl} + 1} - \frac{m_k (A_{kl}^{-1} A_k M A_l A_{kl}^{-1})_{11} - m_l (A_{kl}^{-1} A_k M A_l A_{kl}^{-1})_{11}}{m_{kl} + 1} \right] S_{kl}.
\]

(2.138)

2.7.3 Potential energy

We will derive the potential energy components by finding the integral \( R_{ij}^{kl} = \langle 1/r_{ij} \rangle \).

There are two cases, \( m_{kl} \) even and \( m_{kl} \) odd.

Let us first introduce some simplifying definitions:

\[
a = \text{tr} \left[ J_{11} A_{kl}^{-1} \right],
\]

(2.139)

\[
b = \text{tr} \left[ J_{ij} A_{kl}^{-1} \right],
\]

(2.140)

\[
c = \text{tr} \left[ J_{11} A_{kl}^{-1} J_{ij} A_{kl}^{-1} \right],
\]

(2.141)

which for implementation purposes can be written as

\[
a = (A_{kl}^{-1})_{11},
\]

(2.142)

\[
b = \begin{cases} 
(A_{kl}^{-1})_{ii}, & i = j \\
(A_{kl}^{-1})_{ii} + (A_{kl}^{-1})_{jj} - 2 (A_{kl}^{-1})_{ij}, & i \neq j
\end{cases}
\]

(2.143)

and

\[
c = \begin{cases} 
(A_{kl}^{-1})_{1i}^2, & i = j \\
\left( (A_{kl}^{-1})_{1i} - (A_{kl}^{-1})_{ji} \right)^2, & i \neq j
\end{cases}
\]

(2.144)

Let \( m_{kl} \) be even. If \( p = m_{kl}/2 \) with \( p = 0, 1, 2, \ldots \), then

\[
\langle \varphi_k | 1/r_{ij} | \varphi_l \rangle = \langle \phi_k | r_1^{2p}/r_{ij} | \phi_l \rangle.
\]

(2.145)

Using an integral transformation for \( 1/r_{ij} \),

\[
\langle \varphi_k | 1/r_{ij} | \varphi_l \rangle = \frac{2}{\sqrt{\pi}} \int_0^\infty \langle \varphi_k | \exp \left[ -v^2 r' J_{ij} r \right] | \varphi_l \rangle \, dv,
\]

(2.146)
followed by a differential transformation for \( r_1^{2p} \), and integration over \( r \), we have:
\[
\langle \phi_k | \frac{1}{r_{ij}} | \phi_l \rangle = \frac{2}{\sqrt{\pi}} (-1)^p \int_0^\infty \langle \phi_k | \frac{\partial^p}{\partial u^p} \exp \left[ -u \, r' J_{11} r \right] \exp \left[ -v^2 \, r' J_{ij} r \right] | \phi_l \rangle \, dv \bigg|_{u=0}
\]
\[
= \frac{2}{\sqrt{\pi}} (-1)^p \frac{\partial^p}{\partial u^p} \int_0^\infty \int_{-\infty}^\infty \exp \left[ -r' \left( A_{kl} + u \, J_{11} + v^2 \, J_{ij} \right) r \right] d r \, dv \bigg|_{u=0}
\]
\[
= \frac{2}{\sqrt{\pi}} (-1)^p \frac{\partial^p}{\partial u^p} \int_0^\infty \frac{\pi^{3n/2}}{|A_{kl} + u \, J_{11} + v^2 \, J_{ij}|^{3/2}} \, dv \bigg|_{u=0}
\]
\[
= \frac{2}{\sqrt{\pi}} \langle \phi_k | \phi_l \rangle (-1)^p \frac{\partial^p}{\partial u^p} \int_0^\infty \frac{1}{I_n + u \, J_{11} A_{kl}^{-1} + v^2 \, J_{ij} A_{kl}^{-1}} \, dv \bigg|_{u=0}.
\] (2.147)

Now, since \( J_{11} \) and \( J_{ij} \) are rank one matrices, we can write the determinant in the integral above as a polynomial in the traces we defined in \((2.139, 2.140, 2.141)\) and then integrate over \( v \), yielding
\[
\langle \phi_k | \frac{1}{r_{ij}} | \phi_l \rangle = \frac{2}{\sqrt{\pi}} \langle \phi_k | \phi_l \rangle (-1)^p \frac{\partial^p}{\partial u^p} \int_0^\infty \frac{1}{(1 + u \, a + v^2 b + u v^2 (a b - c))^{3/2}} \, dv \bigg|_{u=0}
\]
\[
= \frac{2}{\sqrt{\pi}} \langle \phi_k | \phi_l \rangle (-1)^p \frac{\partial^p}{\partial u^p} \frac{1}{(1 + a u) (b + u (a b - c))^{1/2}} \bigg|_{u=0}.
\] (2.148)

Then, differentiating \( p \) times with respect to \( u \), setting \( u \) to zero and simplifying gives the final result,
\[
R_{kl}^{ij} = S_{kl} \frac{\gamma_2 (p)}{\sqrt{b}} \sum_{q=0}^p \frac{\gamma_3 (q)}{1 - \frac{c}{a b}} q^q,
\] (2.149)
where
\[
\gamma_2 (p) = \frac{\Gamma (p + 1)}{\Gamma (p + 3/2)}
\] (2.150)
and
\[
\gamma_3 (q) = \frac{\Gamma (q + 1/2)}{\Gamma (q + 1/2) \Gamma (1/2)}.
\] (2.151)

The case when \( m_{kl} \) is odd involves an additional integral transformation, which unfortunately makes these terms somewhat more complicated. The integral evaluation is similar to that for the even case and proceeds as follows.
Let \((m_{kl} + 1)/2 = p\) with \(p = 1, 2, 3, \ldots\), then

\[
\langle \varphi_k \mid 1/r_{ij} \mid \varphi_l \rangle = \langle \phi_k \mid r_1^{2p-1}/r_{ij} \mid \phi_l \rangle = \left\langle \phi_k \mid r_1^{2p} \right. \left. r_{ij} \mid \phi_l \right\rangle.
\]

(2.152)

Making transformations as for the even case, but with the addition of an extra integral transformation for \(1/r_1\) we obtain,

\[
\langle \varphi_k \mid 1/r_{ij} \mid \varphi_l \rangle = \left( \frac{2}{\sqrt{\pi}} \right)^2 (-1)^p
\times \int_0^\infty \int_0^\infty \langle \phi_k \mid \frac{\partial}{\partial u^p} \exp \left[-ur'J_{11}r \right] \exp \left[-w^2r'J_{ij}r \right] \mid \phi_l \rangle \; d\;w \; d\;v |_{u=0}

= \frac{4}{\pi} (-1)^p \frac{\partial}{\partial u^p} \int_0^\infty \int_0^\infty \exp \left[-r' \left(A_{kl} + uJ_{11} + w^2J_{1j} + v^2J_{ij} \right) r \right] \; d\;r \; d\;w \; d\;v |_{u=0}

= \frac{4}{\pi} \langle \phi_k \mid \phi_l \rangle (-1)^p \frac{\partial}{\partial u^p} \int_0^\infty \int_0^\infty \frac{1}{I_n + (u + w^2)J_{11}A_{kl}^{-1} + v^2J_{ij}A_{ij}^{-1}} \frac{3}{2} \; d\;w \; d\;v |_{u=0}.
\]

(2.153)

Again, reducing the determinant to a polynomial in traces and integrating gives

\[
\langle \varphi_k \mid 1/r_{ij} \mid \varphi_l \rangle = \frac{4}{\pi} \langle \phi_k \mid \phi_l \rangle (-1)^p \frac{\partial}{\partial u^p} \int_0^\infty \int_0^\infty \frac{1}{(1 + (u + w^2) a + v^2b + uv^2 (ab - c))^3/2} \; d\;w \; d\;v |_{u=0}

= \frac{4}{\pi} \langle \phi_k \mid \phi_l \rangle (-1)^p \frac{\partial}{\partial u^p} \int_0^\infty \frac{1}{(1 + a (u + w^2)) (b + (u + w^2) (ab - c))^{1/2}} \; d\;w |_{u=0}

= \frac{4}{\pi} \langle \phi_k \mid \phi_l \rangle (-1)^p \frac{\partial}{\partial u^p} \left( c (1 + aw)^{1/2} \right) \arcsin \left[ \left( \frac{c}{a (b + u (ab - c))} \right) \right]^{1/2} |_{u=0}.
\]

(2.154)

Differentiating and simplifying gives the final result for odd \(m_k\) values:

\[
R_{kl}^{ij} = \frac{2}{\sqrt{\pi}} S_{kl} \sqrt{a}
\times \left[ \gamma_3(p) \frac{\arcsin \left( \frac{x}{\sqrt{ab}} \right)}{\sqrt{c}} + \frac{1}{2\sqrt{ab} - c} \sum_{q=1}^{p} \sum_{t=0}^{q-1} \frac{1}{q} \gamma_3(p-q) \gamma_3(t) \left( 1 - \frac{c}{ab} \right)^{q-t} \right].
\]

(2.155)
The inclusion of the arcsin and the double summation in this formula unfortunately complicates these odd power terms compared to the even power case. The implementation of odd powers \( m_k \) requires significantly more computer time due to the complexity of this formula. Furthermore, we found that variation of near optimal \( m_k \) by plus or minus one had negligible effect on energy convergence. Therefore, in our calculations utilizing gradient formulas for energy optimization, we excluded the odd power case.

2.7.4 Matrix elements of interparticle distances

The matrix elements of \( r_1 \) and \( r_1^2 \), which in the case of a diatomic molecule are the internuclear distance and its square, can be obtained using relationship (2.61), in exactly the same manner as we evaluated the overlap:

\[
\langle \varphi_k | r_1^m | \varphi_l \rangle = \langle \phi_k | r_1^m | \phi_l \rangle = \frac{2}{\sqrt{\pi}} \frac{\Gamma\left(\frac{m_k}{2} + \frac{5}{2}\right)}{\Gamma\left(\frac{m_k}{2} + 2\right)} \frac{2}{\sqrt{\pi}} \frac{\Gamma\left(\frac{m_k}{2} + \frac{5}{2}\right)}{\Gamma\left(\frac{m_k}{2} + 2\right)} \frac{\Gamma\left(\frac{m_k}{2} + \frac{5}{2}\right)}{\Gamma\left(\frac{m_k}{2} + 2\right)}
\]

\[
\langle \varphi_k | r_1^m | \varphi_l \rangle = \langle \phi_k | r_1^m | \phi_l \rangle = \frac{2}{\sqrt{\pi}} \frac{\Gamma\left(\frac{m_k}{2} + \frac{5}{2}\right)}{\Gamma\left(\frac{m_k}{2} + 2\right)} \frac{2}{\sqrt{\pi}} \frac{\Gamma\left(\frac{m_k}{2} + \frac{5}{2}\right)}{\Gamma\left(\frac{m_k}{2} + 2\right)} \frac{\Gamma\left(\frac{m_k}{2} + \frac{5}{2}\right)}{\Gamma\left(\frac{m_k}{2} + 2\right)}
\]

The evaluation of the expectation values of other than \( r_1 \) distances and their squares can be done by differentiating expressions (2.149) and (2.124) respectively. We will restrict ourselves with the case when \( m_k \)'s are even, so that \( p = m_k/2 \) with \( p = 0, 1, 2, \ldots \). Let us first consider the simpler case of \( r_{ij}^2 \):

\[
\langle \varphi_k | r_{ij}^2 | \varphi_l \rangle = -\frac{\partial}{\partial u} \langle \varphi_k | \exp[-u r' J_{ij} r] | \varphi_l \rangle \bigg|_{u=0} = -\frac{\partial}{\partial u} \frac{2}{\sqrt{\pi}} \frac{\Gamma\left(p + \frac{3}{2}\right)}{\Gamma\left(p + 1\right)} \frac{2}{\sqrt{\pi}} \frac{\Gamma\left(p + \frac{3}{2}\right)}{\Gamma\left(p + 1\right)} \bigg|_{u=0}.
\]

Here, we will need some simple facts from matrix differential calculus. If \( X \) is a matrix variable and \( \beta \) is a parameter that \( X \) depends on, then

\[
\frac{\partial |X|}{\partial \beta} = |X| \text{tr} \left[ X^{-1} \frac{\partial X}{\partial \beta} \right],
\]

(2.159)
\[ \frac{\partial \text{tr}[X]}{\partial \beta} = \text{tr} \left[ \frac{\partial X}{\partial \beta} \right], \tag{2.160} \]

\[ \frac{\partial (X^{-1})}{\partial \beta} = -X^{-1} \frac{\partial X}{\partial \beta} X^{-1}. \tag{2.161} \]

Using these formulae one can show that

\[ \frac{\partial}{\partial u} \text{tr}[(A_{kl} + uJ_{ij})^{-1} J_{11}] = -\text{tr}[(A_{kl} + uJ_{ij})^{-1} J_{ij}(A_{kl} + uJ_{ij})^{-1} J_{11}] \tag{2.162} \]

and

\[ \langle \varphi_k | r_{ij}^2 | \varphi_l \rangle = \langle \varphi_k | \varphi_l \rangle \left( p \frac{c}{a} + \frac{3}{2} b \right). \tag{2.163} \]

In the same manner for the first power of \( r_{ij} \) one obtains:

\[ \langle \varphi_k | r_{ij} | \varphi_l \rangle = -\langle \varphi_k | r_{ij} | \varphi_l \rangle \left( p \frac{c}{a} + \frac{3}{2} b \right) \]

\[ -\langle \varphi_k | \varphi_l \rangle \gamma_2(p) \sqrt{b} \sum_{q=1}^{p} \gamma_3(q) q \left( 1 - \frac{c}{ab} \right) q^{-1}, \tag{2.164} \]

where

\[ h = \text{tr}[A_{kl}^{-1} J_{ij} A_{kl}^{-1} J_{ij}] = b^2, \]

\[ t = \text{tr}[A_{kl}^{-1} J_{ij} A_{kl}^{-1} J_{ij} A_{kl}^{-1} J_{11}] = bc. \]

After simplification expression (2.164) takes the final form:

\[ \langle \varphi_k | r_{ij} | \varphi_l \rangle = \langle \varphi_k | 1/r_{ij} | \varphi_l \rangle \left( p \frac{c}{a} + b \right) - \langle \varphi_k | \varphi_l \rangle \gamma_2(p) \frac{c}{a} \sum_{q=1}^{p} \gamma_3(q) q \left( 1 - \frac{c}{ab} \right) q^{-1}. \tag{2.165} \]
2.7.5 Nucleus–nucleus correlation function and delta functions

In order to perform calculations of the correlation function of particles 1 and 2 (recall that these are assumed to be nuclei in a diatomic molecule) using basis (2.122), we need the matrix elements of the delta function, \( \delta(r_1 - \xi) \). They can be evaluated by replacing \( \tilde{C}_{kl} \rightarrow A_{kl} + uJ_{11} \) in expression (2.57) and then differentiating \( p \) times with respect to \( u \) at point \( u = 0 \).

\[
\langle \varphi_k | \delta(r_1 - \xi) | \varphi_l \rangle = (-1)^p \frac{\partial^p}{\partial u^p} \frac{\pi^{3n/2}}{[A_{kl} + uJ_{11}]^{3/2} \pi^{3/2} \text{tr}[(A_{kl} + uJ_{11})^{-1}J_{11}]^{3/2}} \frac{1}{\pi} \left[ \frac{\xi^2}{\text{tr}[(A_{kl} + uJ_{11})^{-1}J_{11}]} \right]_{u=0}^p \exp \left[ -\frac{\xi^2}{\text{tr}[(A_{kl} + uJ_{11})^{-1}J_{11}]} \right] .
\]

Applying formula (2.162) and using the fact that \( \text{tr}[XJ_{ii}XJ_{ii}] = \text{tr}[XJ_{ii}]^2 \) for an arbitrary matrix \( X \) reduces the final result to

\[
\langle \varphi_k | \delta(r_{ij}) | \varphi_l \rangle = \langle \varphi_k | \varphi_l \rangle \frac{1}{2\pi \Gamma(p + \frac{3}{2})} \left( A_{kl}^{-1}\right)_{11}^{3/2} \left( A_{kl}^{-1} \right)_{11}^{p} \exp \left[ -\frac{\xi^2}{\left( A_{kl}^{-1} \right)_{11}} \right] .
\]

(2.166)

The matrix elements of \( \delta(r_{ij}) \) for \( j \neq i = 1, 2, \ldots, n \) and \( \delta(r_i), i \neq 1 \) can be easily obtained by straightforward integration. The procedure is very similar to the evaluation of the overlap integral and yields

\[
\langle \varphi_k | \delta(r_{ij}) | \varphi_l \rangle = \frac{2}{\sqrt{\pi}} \Gamma \left( p + \frac{3}{2} \right) \left( D_{kl}^{-1}\right)_{11}^{p} \frac{\pi^{3(n-1)/2}}{\left| D_{kl} \right|^{3/2}} \left( \frac{\left| A_{kl} \right|}{\left| D_{kl} \right|} \right)^{3/2} \left( \frac{\left( D_{kl}^{-1}\right)_{11}}{\left( A_{kl}^{-1} \right)_{11}} \right)^p ,
\]

(2.167)

where \( D_{kl} \) is an \((n-1) \times (n-1)\) matrix formed from \( A_{kl} \) by adding the \( j \)-th row to the \( i \)-th one, then adding \( j \)-th column to the \( i \)-th column, and then crossing out the \( j \)-th column and row.

In the case of \( \delta(r_i), i \neq 1 \) the expression is the same as (2.167), but matrix \( D_{kl} \) is formed from \( A_{kl} \) by simply crossing out the \( i \)-th column and \( i \)-th row (without prior additions).

To obtain matrix elements of \( \delta(r_1) \) one needs to set \( \xi = 0 \) in (2.166). These matrix elements are nonzeros only when \( p \neq 0 \).
2.7.6 Energy gradient

We would like to note that only one term in the symmetry projection will be represented. As was the case for the integral formulas, the symmetry terms require the substitution $A_l \mapsto P'A_lP = P'L_l (P'L_l)'$ or more generally, $L_l \mapsto P'L_l$. This is required for derivatives with respect to both vech $[L_k]$ and vech $[L_l]$. The derivatives with respect to vech $[L_l]$ will require further modification and this will be noted in the formulae below.

Using the normalized overlap formula, eqn (2.125), the derivative with respect to the nonzero terms of the lower triangular matrix $L_k$ is

$$
\frac{\partial S_{kl}}{\partial \text{vech } L_k} = \frac{3}{2} S_{kl} \text{vech } \left[ (L_k^{-1})' - 2A_k^{-1}L_k \right]' + S_{kl} \frac{m_k}{(A_k^{-1})_{11}} \text{vech } \left[ A^{-1}_{kl}J_{11}A^{-1}_{kl}L_k \right]' - S_{kl} \frac{m_{kl}}{(A^{-1}_{kl})_{11}} \text{vech } \left[ A^{-1}_{kl}J_{11}A^{-1}_{kl}L_l \right]' .
$$

(2.168)

For the derivative with respect to the elements vech $L_l$, we account for the symmetry terms by making a multiplication by $P$ in addition to the substitutions described above. Thus,

$$
\frac{\partial S_{kl}}{\partial \text{vech } L_l} = \frac{3}{2} S_{kl} \text{vech } \left[ P(L_l^{-1})' - 2PA_k^{-1}L_l \right]' + S_{kl} \frac{m_l}{(A_l^{-1})_{11}} \text{vech } \left[ PA_l^{-1}J_{11}A_l^{-1}L_l \right]' - S_{kl} \frac{m_{kl}}{(A_l^{-1})_{11}} \text{vech } \left[ PA_{kl}^{-1}J_{11}A_{kl}^{-1}L_l \right]' .
$$

(2.169)

The kinetic energy gradient components are obtained by differentiating equation
(2.138) with respect to vech \( L_k \) and vech \( L_l \):

\[
\frac{\partial T_{kl}}{\partial (\text{vech} \ L_k)} = \frac{\partial S_{kl}}{\partial (\text{vech} \ L_k)} \frac{T_{kl}}{S_{kl}} + 2S_{kl} \left[ 6 \text{vech} \left[ A_{kl}^{-1} A_l M A_k A_{kl}^{-1} L_k \right]' \right. \\
+ 2 \left( A_{kl}^{-1} \right)_{11}^{-2} \left( \frac{m_k m_l M_{11}}{m_k + 1} - m_k \left( A_{kl}^{-1} A_l M A_k A_{kl}^{-1} \right)_{11} - m_l \left( A_{kl}^{-1} A_k M A_k A_{kl}^{-1} \right)_{11} \right) \\
\times \text{vech} \left[ A_{kl}^{-1} J_{11} A_{kl}^{-1} L_k \right]' \\
- 2 \left( A_{kl}^{-1} \right)_{11}^{-1} m_l \text{vech} \left[ A_{kl}^{-1} J_{11} A_{kl}^{-1} A_k M A_l A_{kl}^{-1} L_k + A_{kl}^{-1} A_l M A_k A_{kl}^{-1} J_{11} A_{kl}^{-1} L_k \right] \\
\left. + 2 \left( A_{kl}^{-1} \right)_{11}^{-1} m_k \text{vech} \left[ A_{kl}^{-1} J_{11} A_{kl}^{-1} A_l M A_k A_{kl}^{-1} L_k + A_{kl}^{-1} A_k M A_l A_{kl}^{-1} J_{11} A_{kl}^{-1} L_k \right] \right],
\tag{2.170}
\]

and the derivative with respect to vech \( L_l \) including a symmetry projector term \( P \) is given by

\[
\frac{\partial T_{kl}}{\partial (\text{vech} \ L_l)} = \frac{\partial S_{kl}}{\partial (\text{vech} \ L_l)} \frac{T_{kl}}{S_{kl}} + 2S_{kl} \left[ 6 \text{vech} \left[ PA_{kl}^{-1} A_k M A_k A_{kl}^{-1} L_l \right]' \right. \\
+ 2 \left( A_{kl}^{-1} \right)_{11}^{-2} \left( \frac{m_k m_l M_{11}}{m_k + 1} - m_k \left( A_{kl}^{-1} A_l M A_k A_{kl}^{-1} \right)_{11} - m_l \left( A_{kl}^{-1} A_k M A_k A_{kl}^{-1} \right)_{11} \right) \\
\times \text{vech} \left[ PA_{kl}^{-1} J_{11} A_{kl}^{-1} L_l \right]' \\
- 2 \left( A_{kl}^{-1} \right)_{11}^{-1} m_k \text{vech} \left[ PA_{kl}^{-1} J_{11} A_{kl}^{-1} A_l M A_k A_{kl}^{-1} L_l + PA_{kl}^{-1} A_k M A_l A_{kl}^{-1} J_{11} A_{kl}^{-1} L_l \right] \\
\left. + 2 \left( A_{kl}^{-1} \right)_{11}^{-1} m_l \text{vech} \left[ PA_{kl}^{-1} J_{11} A_{kl}^{-1} A_l M A_k A_{kl}^{-1} L_l + PA_{kl}^{-1} A_k M A_l A_{kl}^{-1} J_{11} A_{kl}^{-1} L_l \right] \right].
\tag{2.171}
\]

Using the even \( m_k \) potential energy integral formula, eqn(2.149), the definitions for \( a, b, \) and \( c \) given in eqns(2.139,2.140,2.141), and the definitions for \( \gamma_2 \) and \( \gamma_3 \) given in equations (2.150,2.151), the gradient terms for the potential energy, with
\[ m_{kl} = 2p, \] are given by
\[
\frac{\partial R_{kl}^{ij}}{\partial (\text{vech } L_k)^T} = \frac{\partial S_{kl}}{\partial (\text{vech } L_k)^T} S_{kl} - \frac{\partial b}{\partial (\text{vech } L_k)^T} R_{kl}^{ij} + \gamma_2 (p) S_{kl} b^{-1/2}
\times \left[ \sum_{q=1}^{p} \gamma_3 (q) q \left( 1 - \frac{c}{ab} \right)^{q-1} \frac{c}{(ab)^q} \left( \frac{\partial a}{\partial (\text{vech } L_k)^T} b + a \frac{\partial b}{\partial (\text{vech } L_k)^T} - \frac{ab}{c} \frac{\partial c}{\partial (\text{vech } L_k)^T} \right) \right],
\tag{2.172}
\]
where
\[
\frac{\partial a}{\partial (\text{vech } L_k)^T} = -2 \text{vech} \left[ A_{kl}^{-1} J_{11} A_{kl}^{-1} L_k \right],
\tag{2.173}
\]
and
\[
\frac{\partial b}{\partial (\text{vech } L_k)^T} = -2 \text{vech} \left[ A_{kl}^{-1} J_{ij} A_{kl}^{-1} L_k \right],
\tag{2.174}
\]
and
\[
\frac{\partial c}{\partial (\text{vech } L_k)^T} = -2 \text{vech} \left[ A_{kl}^{-1} J_{11} A_{kl}^{-1} J_{ij} A_{kl}^{-1} L_k \right] - 2 \text{vech} \left[ A_{kl}^{-1} J_{ij} A_{kl}^{-1} J_{11} A_{kl}^{-1} L_k \right] - 2 \text{vech} \left[ P A_{kl}^{-1} \cdots \right].
\tag{2.175}
\]

The derivative with respect to \( \text{vech } L_l \) has the same form as the above but with \( L_k \) replaced by \( P' L_l \) and each of the expressions \( \text{vech} \left[ A_{kl}^{-1} \cdots \right] \) replaced by \( \text{vech} \left[ P A_{kl}^{-1} \cdots \right] \).

### 2.8 Relativistic corrections

As it has been mentioned in the chapter 1, the accuracy of modern gas phase measurements is extremely high. In order to match the experimental transition energies it is often not sufficient to account only for the nonadiabatic effects. The second factor that is responsible for the discrepancy between the theory and the experiment is relativistic and, to a lesser extent, QED effects. In this section we would like to touch this subject in the context of variational calculations with explicitly correlated Gaussians. The development of the methods that allow evaluation of relativistic corrections with the Gaussian basis functions (2.22) is being done in a collaboration of our laboratory at Arizona with colleagues at university of Torun (Poland). The work on this project is still under way and only some part of relevant
material can be included in this dissertation. It mainly concerns the mass-velocity and Darwin corrections.

In general, it is not possible to take the Dirac relativistic Hamiltonian and separate it into nonrelativistic and relativistic parts. The simplest and most traditional way to calculate the relativistic effects in atomic and molecular systems is based on the Pauli approximation. It provides a framework for describing a quantum particle with the accuracy of the order of $\alpha^2$, where $\alpha$ is the fine structure constant. To get a more accurate description of a quantum system going beyond the Pauli approximation one can use the Breit–Pauli equation \[ \text{[39]}, \] which explicitly includes operators describing the orbit–orbit and spin–orbit interactions, as well as other two–particle magnetic interactions. However, since the Breit–Pauli equation is not completely invariant with respect to the Lorentz transformation, an approximation is introduced in the calculation of the relativistic effects.

The Pauli approximation describes a state of a quantum particle represented by a two–component wave function, which is an eigenfunction of the nonrelativistic Hamiltonian. In such an approach the relativistic effects (and their corresponding operators) must be treated as perturbations and determined as the first order corrections to the nonrelativistic energy.

In the calculation of the mass–velocity (MV) and the Darwin (D) relativistic effects, we start with respective Hamiltonians in the laboratory coordinate frame ($\mathbf{R}$):

\begin{align}
\hat{H}_{\text{MV}} &= -\frac{\alpha^2}{8} \sum_{i=1}^{N} \frac{1}{M_i^3} \nabla^4_{\mathbf{R}_i}, \quad \tag{2.176} \\
\hat{H}_D &= \frac{\alpha^2}{8} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \frac{1}{M_i^2} \nabla^2_{\mathbf{R}_i} \frac{Q_i Q_j}{R_{ij}}. \quad \tag{2.177}
\end{align}

Upon the transformation of the laboratory coordinate system to the internal system, the Darwin Hamiltonian (2.177) separates into a term dependent on the position vector of the center of mass in the laboratory frame, $\mathbf{r}_0$, and a term dependent on the internal coordinates, $\{\mathbf{r}\} = \{\mathbf{r}'_1, \mathbf{r}'_2, \ldots, \mathbf{r}'_n\}$:

\begin{align}
\hat{H}_D(\mathbf{r}, \mathbf{r}_0) &= \hat{H}_D(\mathbf{r}_0) + \hat{H}_D(\mathbf{r}) \quad \tag{2.178}
\end{align}
where:

\[ \hat{H}_D(r_0) = \frac{\alpha^2}{4m_0} \nabla^2 r_0 V(r) = 0, \]  
(2.179)

because \( V(r) \) is independent of \( r_0 \), and where

\[ \hat{H}_D(r) = \frac{\alpha^2}{8} \left[ \sum_{i=1}^{n} \left( \frac{1}{M_i^2} + \frac{1}{M_{i+1}^2} \right) \nabla^2_{r_i} q_0 q_i + \sum_{i=1}^{n} \sum_{j \neq i}^{n} \frac{1}{M_{i+1}^2} \nabla^2_{r_i} q_i q_j \right]. \]  
(2.180)

The Darwin correction can be calculated either directly using the operator (2.180), \( \hat{H}_D(r) = \hat{H}_D(r) \) (we will call it here the first approach), or using an operator obtained from (2.180) by applying the Poisson equations (the second approach):

\[ \nabla^2_{r_i} \frac{1}{r_i} = -4\pi \delta(r_i), \quad \nabla^2_{r_i} \frac{1}{r_{ij}} = \nabla^2_{r_{ij}} \frac{1}{r_{ij}} = -4\pi \delta(r_{ij}). \]  
(2.181)

This results in the Darwin Hamiltonian in the following form:

\[ \hat{H}_D^{II}(r) = -\frac{\pi \alpha^2}{2} \left[ \sum_{i=1}^{n} \left( \frac{1}{M_i^2} + \frac{1}{M_{i+1}^2} \right) q_0 q_i \delta(r_i) + \sum_{i=1}^{n} \sum_{j \neq i}^{n} \frac{1}{M_{i+1}^2} q_i q_j \delta(r_{ij}) \right]. \]  
(2.182)

In the calculation presented later in chapter 4 we used both Darwin Hamiltonians, \( \hat{H}_D^I(r) \) and \( \hat{H}_D^{II}(r) \). This was done to make sure that the algorithm for calculating the Darwin corrections was correctly implemented.

Upon the transformation of the coordinate system (\( \{ \mathbf{R} \} \rightarrow \{ \mathbf{r}_0, \mathbf{r}' \} \)) the mass–velocity Hamiltonian can be represented as a sum of three terms:

\[ \hat{H}_{MV}(\mathbf{r}, \mathbf{r}_0) = \hat{H}_{MV}(\mathbf{r}_0) + \hat{H}_{MV}(\mathbf{r}) + \hat{H}_{MV}^{coupl}(\mathbf{r}_0, \mathbf{r}), \]  
(2.183)

where the term \( \hat{H}_{MV}(\mathbf{r}) \) relevant to the present calculations of the relativistic contribution to the internal energy has the form:

\[ \hat{H}_{MV}(\mathbf{r}) = -\frac{\alpha^2}{8} \left[ \sum_{i=1}^{n} \left( \nabla_{r_i} \right)^4 + \sum_{i=1}^{n} \frac{1}{M_{i+1}^2} \nabla^4_{r_i} \right]. \]  
(2.184)

The last term in equation (2.183), \( \hat{H}_{MV}^{coupl}(\mathbf{r}_0, \mathbf{r}) \), describes relativistic coupling between the motion of the center of mass and the internal motion. This effect was not considered in our calculations as we assume that the system as a whole is at rest, i.e. the center of mass is not moving.
The calculation of the mass-velocity and Darwin relativistic correction to the energy of the internal motion of the system was performed for each state using the first order perturbation theory as the expectation value of the Hamiltonian representing the internal mass–velocity and Darwin contributions:

\[ \hat{H}'(\mathbf{r}) = \hat{H}_{\text{MV}}(\mathbf{r}) + \hat{H}_{\text{D}}(\mathbf{r}). \] (2.185)

More details on computing these corrections can be found in [28, 29, 30].

It should be mentioned that the mass-velocity and Darwin corrections, which we have included in our calculations, alone cannot provide drastic improvement in the agreement between the theory and the experiment. There are other relativistic corrections that may be somewhat smaller in absolute values, but have the same order of magnitude. These are orbit–orbit, spin-spin, and spin-orbit (the latter should be small for systems with only \( \sigma \)-electrons). In general, the leading terms of relativistic corrections (if not vanished) are proportional to \( \alpha^2 \). In addition to that, there are QED corrections, whose leading terms are proportional to \( \alpha^3 \). To get an idea how the above mentioned terms could contribute to the total energy we can refer to work [40], where the relativistic and QED effects are taken into account or at least estimated for the hydrogen molecule by means of correcting the BO potential energy curve. It is sufficient for our purpose to know the numbers approximately. Thus, we can restrict ourselves by considering the relativistic and QED effects at equilibrium internuclear separation of 1.4 a.u. (not vibrationally averaged). The contributions have approximately the following magnitudes: 17 cm\(^{-1} \) (mass–velocity), 0.5 cm\(^{-1} \) (orbit–orbit), 15 cm\(^{-1} \) (Darwin), 1 cm\(^{-1} \) (spin–spin), 0.7 cm\(^{-1} \) (radiative correction). The numbers seem to be quite large, but we should not forget that when making comparison with the experiment we use differences in the total energies of different vibrational levels. As a result of the subtractions, the relativistic and QED corrections cancel each other significantly (see chapter 4, in particular section 4.1). The final differences in the nonrelativistic and relativistic transition energies are of the order of 0.1 cm\(^{-1} \). From here it is easy to mistakenly conclude that there is no need to require accuracy of the nonrelativistic energy that
exceeds $10^{-7}$ a.u. in order to make a meaningful comparison with the experiment. In reality it is not correct. We should take into account the fact that the expectation values that appear in the operators corresponding to the relativistic corrections may converge much slower than the energy (this is because the quantity that is minimized in variational calculations is the energy). In fact, the expectation values of such quantities as Dirac delta functions or the forth power of the momentum do converge very slowly compared to the energy due to peculiarities of Gaussian basis functions. That is why it is very desirable to obtain as accurate nonrelativistic solution as possible.

Lastly, we would like to say that both relativistic and radiative corrections scale as $Z^4$ in atoms, where $Z$ is the nuclear charge, while the nonrelativistic energy scales as $Z^2$ only. This should also take place in the case of molecules. It means that for molecules with larger nuclear charges these corrections become more prominent.
CHAPTER 3

IMPLEMENTATION ON PARALLEL COMPUTER SYSTEMS

Due to peculiarities of quantum chemistry applications, almost any theoretical development in this branch of science is done with a thought of its subsequent computer implementation in mind. It is well known that the vast majority of quantum chemical problems are solved using computers. Moreover, the computational power required for up-to-date calculations is often very significant and, correspondingly, costly. Quantum chemistry has been one of the major consumers of scientific computing resources for several decades. Considering the high computational demands raised by quantum chemical problems, it is not a surprise that an efficient “translation” of purely theoretical developments into a computer code plays a crucial role. In fact, many quantum chemists nowadays spend a great amount of time working on problems related to computer coding and numerical implementation rather than pure theory. This work is often quite complex and contains a lot of small details that, combined, provide the high efficiency of the calculations. The numerical implementation of the variational methods for non-BO calculations is not an exception, despite their very simple theoretical formulation. It is not possible to consider every single nuance of this work in this dissertation. However, not considering such an important part of the research at all would leave a big gap between the bare formulae and the final results presented in the dissertation. Therefore, in this chapter we will present some amount of appropriate material that, in our view, gives a notion of what kind of problems one faces when implementing variational methods numerically.
3.1 General remarks

As was mentioned before, the non-BO calculations typically require high accuracy and, as a sequence, a great amount of computer time. The way to partially overcome this problem of high computational demands is extensive parallelization of the computer code for use on multinode computational systems. Indeed, taking advantage of the power of modern parallel computers may speed up the calculations by a very significant factor or give a possibility to study more complex systems. This has been backed up by recent advances in both hardware and software for parallel computations. There is a reason to think that parallel implementation of computational algorithms will be becoming more and more important in the future because parallel computer systems are expected to be cheaper and widely available. In addition to that, there is a tendency in the modern chip development to boost the general performance by making several cores in a single central processor unit (CPU), which, in a way, makes a small parallel supercomputer out of each CPU.

As far as software component is concerned, there are several concepts widely used in parallel computations. They all have their area of applicability depending on the type of the problem one solves and the amount of communication between nodes of a parallel computer system. In our code development we made use of MPI (Message Passing Interface) standard. It provides a relatively simple, yet very powerful way to parallelize computations. Besides, MPI software is available for all major hardware platforms, which allows a migration from one computer system to another one with minimal or no modification of the computer code.

The two most time consuming parts of the calculations are the computations of matrix elements of the Hamiltonian and the overlap and the solution of the generalized eigenvalue problem (2.17). The former takes progressively larger percentage of the total time for systems with more particles, especially in the case when there are many identical particles. The latter becomes the most time consuming for small systems, such as three-particle HD\(^+\), and, also, for any system when the number of basis functions is very large. It should be noted that each of these tasks must be
repeated routinely an enormous number of times if one aims for very high precision of the final results, and, as a sequence, has to use large basis sets (we are talking about millions of repetitions). The main reason for that is the optimization of non-linear variational parameters of the basis functions. It is obvious that to achieve high efficiency of the calculations, they should be very well organized.

The calculation of expectation values, although may require some computer resources, usually is not time consuming compared to the generation of the wave functions as this is only a “single point” calculation. In other words, the calculation of the expectation values such as mean interparticle distances, correlation functions, relativistic corrections, etc. is done only once, in the very end, with the best quality wave function that contains the maximal number of terms (and, maybe, a few more times before, for wave functions with smaller number of terms, if the convergence pattern of the expectation values is needed).

3.2 Computations of matrix elements

The calculation of matrix elements represents a case when computations can be parallelized very effectively. There are very few “bottlenecks” that can significantly reduce the degree of parallelization. We simply divide the matrices of the Hamiltonian, $H$, and the overlap, $S$, in such a way that each process that takes part in the computations is responsible for computing a certain part of those matrices. To divide the labor more evenly, one may also take into account the fact that each matrix elements for a system containing identical particles is a sum of several terms. It is especially useful in the case when the time needed to evaluate a matrix element depends on the actual values of nonlinear variational parameters. Those terms due to indistinguishability of the particles usually require equal amount of computational time and this helps to smooth the statistical difference in the amount of work assigned to each process. Once all matrix elements are computed, all running processes exchange their results to receive a full set of data necessary for further steps. Calculating matrix elements for a single $H$ and $S$ set is usually quite fast unless the
molecule is very large and complex. Thus, the exchange of the results must be done very quickly. The delays caused by this exchange are normally insignificant for most modern parallel computer systems. In contrast, in the “grid”-type networks that have become very popular in recent years, such computations cannot be performed efficiently, because communication delays would be inadmissible long there.

3.3 Linear algebra routines

It is very common that in the process of growing the basis set a point is reached when the total energy is already converged relatively well. When exactly this happens depends on the complexity of the system, but typically a few dozens or hundreds of basis functions is sufficient. After this, the energy is being simply refined. To be more quantitative we can define the meaning of the expression “relatively well converged energy” as follows: the difference between the energy of the state being computed, \( \epsilon_i \), and the exact energy of that state, \( E_i \), is smaller than the distance between the energy level being computed and its neighbors, \( \epsilon_{i+1} \) and \( \epsilon_{i-1} \). When this is the case, one can use the inverse iteration method to solve the generalized eigenvalue problem (2.17). The idea of the method consists in performing the iterations,

\[
(H - \epsilon_{\text{appr}} S) c^{(k+1)} = S c^{(k)}
\]  

(3.1)

where \( \epsilon_{\text{appr}} \) is an approximate value of the exact solution of the generalized symmetric eigenvalue problem. The starting vector \( c^{(0)} \) can be chosen randomly. As long as the exact eigenvalue we need to obtain is closer to \( \epsilon_{\text{appr}} \) than any other eigenvalue, the iterations (3.1) will converge. Typically, just few iterations are needed to find \( \epsilon \) with sufficient accuracy. Each iteration in (3.1) is performed in a few steps:

\[
H - \epsilon_{\text{appr}} S = LDL',
\]  

(3.2)

\[
Lx = Sc^{(k)},
\]  

(3.3)

\[
Dy = x,
\]  

(3.4)

\[
L'c^{(k+1)} = y.
\]  

(3.5)
Here, $L$ is a lower triangular matrix (not to be confused with $L_k$, the Cholesky factor of the matrix of nonlinear parameters $A_k$), and $D$ is a diagonal matrix. Steps (3.3,3.4,3.5) involve solutions of systems of linear equations, while step (3.2) requires a matrix factorization. The above scheme of the solution of the generalized eigenvalue problem has proven to be very efficient and accurate in numerous calculations. But the main advantage of this scheme is revealed when one has to routinely solve the secular equation with only one row and one column of matrices $H$ and $S$ changed, which takes place upon modifying nonlinear parameters of a single basis function. In this case, updating factorization (3.2) requires only $\propto K^2$ arithmetic operations ($K$ is the number of basis functions) while, in general, the solution “from scratch” requires $\propto K^3$ operations. Steps (3.3,3.4,3.5) also require $\propto K^2$ arithmetic operations.

All four steps (3.2,3.3,3.4,3.5) can be programmed in a way suitable for parallel computations. Although the degree of parallelization here is not as high as in the case of matrix element calculation, the speed up gained by using multiple computational nodes scales relatively well as the number of nodes is increased.

### 3.4 Optimization of nonlinear parameters

It is well known that the convergence of variational expansions in terms of correlated Gaussians strongly depends on how one selects the nonlinear parameters in the Gaussian exponentials. In order to get high accuracy results in the calculations, one needs to perform an optimization of those parameters. Since the number of basis functions in non-BO calculations is usually large, the total number of the exponential parameters may reach many thousands. Optimization of this many nonlinear parameters represents a serious computational problem. The two most commonly applied approaches to the parameter optimization are: (a) the full optimization, which is very effective when the analytical gradient of the energy with respect to the parameters is available; (b) the method based on a stochastic selection of the parameters. Method (a) is very efficient for optimization of relatively small basis
sets. However, once the number of basis functions exceeds a few hundreds, it often becomes unacceptably expensive.

We found that in many practical situations a hybrid method that combines the gradient-driven optimization with the stochastic selection method turns out to be very efficient. In this approach, we first generate a relatively small basis set using the full gradient optimization. It provides a good starting point for the next step of the procedure: the energy is already well converged and the trial wave function approximates the exact wave function quite well. This means that the nonlinear parameters of basis functions are distributed over the most important region in the parameter space. In the next step we apply the following strategy. We increase the size of the basis set by including additional basis functions, one by one (in general, it can be a few functions), with randomly selected values of the nonlinear parameters and values of the preexponential powers. More precisely, we generate a set of random candidates and each of these candidates is then tested. The random generation of candidates may be based on the distribution of nonlinear parameters of the functions that have been already included in the basis, which makes this procedure even more flexible. Only the best candidate (or few of them), that is the one that lowers the energy the most is accepted to the basis. Then, after including the function into the basis set, we first optimize the power of its preexponential factor (if there is any) using the finite difference approach. Secondly, we optimize the exponential parameters using the analytical gradient approach. After adding several new basis functions using this scheme (the actual number may vary depending on the desired degree of optimization), the entire basis set is reoptimized by means of the gradient approach applied subsequently to each basis functions, one function at a time. This continues until the number of basis functions reaches a certain limit or until the necessary convergence of the total energy is achieved. The random part of the process described above was originally proposed by Kukulin and Krasnopolsky [41] for few-nucleon problems in nuclear physics and then extensively used by Varga and coworkers [9, 42]. None of them, however, implemented an optimization that uses the analytic energy gradient.
We should note, that in spite of usually high efficiency of the hybrid method, the procedure of basis set building and optimization still requires a lot of computational resources, especially for systems with a large number of particles and a large number of particle permutations in the Young operator. In addition to that, as we found from our experience, a full (simultaneous) optimization of all nonlinear parameters may still be the only practical option in some cases when the Gaussians tend to be very strongly coupled. This may happen, for example, when we deal with highly vibrationally excited states, or when we use complex Gaussians in triatomic calculations.
In this chapter we will illustrate the capabilities of the variational method by showing the results of very accurate non-BO calculations on small molecular systems. These calculations are primarily done using Gaussian basis functions with premultipliers (2.22). Some calculations with complex Gaussian basis functions (2.23) are presented as well. In the course of this presentation we will be having short discussions about the problems that one encounters in such calculations and the physics/chemistry of the systems being considered.

4.1 The ground and excited states of H$_2$

Due to a small number of electrons and nuclei, H$_2$ molecule often serves as the first target for testing different methods in quantum chemistry. Despite the fact that this system has been very well studied since the early days of quantum mechanics and the pioneer’s work of Heitler and London [43], very few studies have been done outside the framework of the Born–Oppenheimer approximation. Moreover, all of the non-BO calculations usually deal with the ground or few low-lying states only. In this part we present highly accurate, non-relativistic, variational, non-BO calculations of the “vibrational spectrum” of the H$_2$ molecule [30]. Although we use the traditional term “vibrational spectrum”, the states we have calculated can be better characterized as states with the zero total angular momentum, which is the sum of the angular momenta of the electrons and the nuclei.

The non-BO wave functions of different excited states have to differ from each other by the number of nodes along the internuclear distance, which in case of basis (2.22) is $r_1$. To accurately describe the nodal structure in all fifteen states considered in our calculations, a wide range of powers, $m_k$, had to be used. While
Table 4.1: Total non-BO energies, $E_{v}^{\text{nonrel}}$, mass–velocity and Darwin relativistic corrections, and total non-BO energy with the relativistic corrections included, $E_{v}^{\text{rel}}$, for H$_2$ computed with 5000 basis functions [30]. All values are in a.u.

<table>
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<th>$v$</th>
<th>$E_{v}^{\text{nonrel}}$</th>
<th>Mass–velocity</th>
<th>Darwin</th>
<th>$E_{v}^{\text{rel}}$</th>
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</thead>
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<td>-8.657522×10$^{-5}$</td>
<td>7.281823×10$^{-5}$</td>
<td>-1.16403878751</td>
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<td>-8.414339×10$^{-5}$</td>
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<td>-1.14507879321</td>
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<tr>
<td>2</td>
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<td>-8.188957×10$^{-5}$</td>
<td>6.867302×10$^{-5}$</td>
<td>-1.12719106004</td>
</tr>
<tr>
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<td>-7.980406×10$^{-5}$</td>
<td>6.689359×10$^{-5}$</td>
<td>-1.1103534331</td>
</tr>
<tr>
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<td>6.523308×10$^{-5}$</td>
<td>-1.09455181188</td>
</tr>
<tr>
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<td>-7.609807×10$^{-5}$</td>
<td>6.364060×10$^{-5}$</td>
<td>-1.0797819521</td>
</tr>
<tr>
<td>6</td>
<td>-1.06603722490</td>
<td>-7.447390×10$^{-5}$</td>
<td>6.216637×10$^{-5}$</td>
<td>-1.06604953243</td>
</tr>
<tr>
<td>7</td>
<td>-1.05336074599</td>
<td>-7.298806×10$^{-5}$</td>
<td>6.079169×10$^{-5}$</td>
<td>-1.05337294236</td>
</tr>
<tr>
<td>8</td>
<td>-1.04177301560</td>
<td>-7.164116×10$^{-5}$</td>
<td>5.951347×10$^{-5}$</td>
<td>-1.04178514329</td>
</tr>
<tr>
<td>9</td>
<td>-1.03132535444</td>
<td>-7.043407×10$^{-5}$</td>
<td>5.832927×10$^{-5}$</td>
<td>-1.03133745925</td>
</tr>
<tr>
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<td>-1.02209235935</td>
<td>-6.936293×10$^{-5}$</td>
<td>5.723048×10$^{-5}$</td>
<td>-1.02210449180</td>
</tr>
<tr>
<td>11</td>
<td>-1.01417901712</td>
<td>-6.843596×10$^{-5}$</td>
<td>5.621885×10$^{-5}$</td>
<td>-1.01419123424</td>
</tr>
<tr>
<td>12</td>
<td>-1.00773106386</td>
<td>-6.766075×10$^{-5}$</td>
<td>5.528758×10$^{-5}$</td>
<td>-1.00774343704</td>
</tr>
<tr>
<td>13</td>
<td>-1.00295034375</td>
<td>-6.704939×10$^{-5}$</td>
<td>5.443745×10$^{-5}$</td>
<td>-1.00296295569</td>
</tr>
<tr>
<td>14</td>
<td>-1.00011590063</td>
<td>-6.659363×10$^{-5}$</td>
<td>5.364734×10$^{-5}$</td>
<td>-1.00012884692</td>
</tr>
<tr>
<td>H+H</td>
<td>-0.99945567942</td>
<td>-6.54970×10$^{-5}$</td>
<td>5.316445×10$^{-5}$</td>
<td>-0.99946906467</td>
</tr>
</tbody>
</table>

in the calculations of the H$_2$ ground state [16], the power range was 0–40, in the present calculations it was extended to 0–250 in order to allow pseudoparticle 1 density (i.e. nucleus–nucleus correlation function) peaks to be more localized and sharp if needed. We should notice that if one aims for highly accurate results for the energy then the wave function of each of the excited states must be obtained in a separate calculation. Thus, the optimization of nonlinear parameters is done independently for each state considered.

The relativistic corrections, the total non-BO energies uncorrected and corrected for the relativistic effects for all 15 vibrational states of H$_2$ obtained with 5000 ECGFs are shown in Table 4.1. The energy for the ground state of $-1.1640250305$ hartree is noticeably lower than the previously reported upper bound of $-1.1640250232$ hartree [16] and lower than $-1.1640250300$ hartree reported in [19]. As one can notice, both mass–velocity and Darwin effects decrease with the vibra-
Table 4.2: Nonrelativistic, non-BO transition energies computed with 5000 basis functions [30], in comparison with the experimental frequencies of Dabrowski [44] and with the nonrelativistic frequencies of Wolniewicz [45]. All values are in cm\(^{-1}\). The values in parantheses are differences with respect to the data in the first column.

<table>
<thead>
<tr>
<th>(v)</th>
<th>(E_{v}^{\text{nonrel}} - E_{v+1}^{\text{nonrel}})</th>
<th>Experiment [44] ((\Delta))</th>
<th>Wolniewicz [45] ((\Delta))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4161.164</td>
<td>4161.14 (0.02)</td>
<td>4161.163 (0.001)</td>
</tr>
<tr>
<td>1</td>
<td>3925.839</td>
<td>3925.79 (0.05)</td>
<td>3925.837 (0.002)</td>
</tr>
<tr>
<td>2</td>
<td>3695.395</td>
<td>3695.43 (-0.03)</td>
<td>3695.392 (0.003)</td>
</tr>
<tr>
<td>3</td>
<td>3467.986</td>
<td>3467.95 (0.04)</td>
<td>3467.983 (0.003)</td>
</tr>
<tr>
<td>4</td>
<td>3241.581</td>
<td>3241.61 (-0.03)</td>
<td>3241.577 (0.004)</td>
</tr>
<tr>
<td>5</td>
<td>3013.872</td>
<td>3013.86 (0.01)</td>
<td>3013.869 (0.003)</td>
</tr>
<tr>
<td>6</td>
<td>2782.166</td>
<td>2782.13 (0.04)</td>
<td>2782.161 (0.005)</td>
</tr>
<tr>
<td>7</td>
<td>2543.213</td>
<td>2543.25 (-0.04)</td>
<td>2543.209 (0.004)</td>
</tr>
<tr>
<td>8</td>
<td>2292.997</td>
<td>2292.93 (0.07)</td>
<td>2292.993 (0.004)</td>
</tr>
<tr>
<td>9</td>
<td>2026.408</td>
<td>2026.38 (0.03)</td>
<td>2026.406 (0.002)</td>
</tr>
<tr>
<td>10</td>
<td>1736.778</td>
<td>1736.66 (0.12)</td>
<td>1736.776 (0.002)</td>
</tr>
<tr>
<td>11</td>
<td>1415.162</td>
<td>1415.07 (0.09)</td>
<td>1415.163 (-0.001)</td>
</tr>
<tr>
<td>12</td>
<td>1049.247</td>
<td>1049.16 (0.09)</td>
<td>1049.250 (-0.003)</td>
</tr>
<tr>
<td>13</td>
<td>622.088</td>
<td>622.02 (0.07)</td>
<td>622.098 (-0.010)</td>
</tr>
</tbody>
</table>

The most reliable experimental results concerning the pure vibrational transitions of H\(_2\) are still those of Dabrowski [44] obtained more than two decades ago. While the accuracy of those results is probably not more than 0.1 cm\(^{-1}\) they are consistently lower than the calculated transitions. The only reason for this discrepancy can be the relativistic effects.

The next set of results is shown in Table 4.2. It includes the data for the vibrational transition energies obtained in this work, as well as the experimental frequencies of Dabrowski [44], and nonrelativistic frequencies computed before by Wolniewicz [45]. The values in parentheses show the difference between our results and the results obtained in the experiment and the calculated results of Wolniewicz,
Table 4.3: Non-BO, nonrelativistic (nonrel) and relativistically corrected (rel) vibrational frequencies $E_{v+1} - E_v$ for $v = 12 \rightarrow 11$, $v = 13 \rightarrow 12$, and $v = 14 \rightarrow 13$ transitions of H$_2$ in comparison with the experimental transitions of Dabrowski [44] and calculated frequencies obtained by Wolniewicz [46] that include relativistic and radiative corrections. All values are in cm$^{-1}$.

<table>
<thead>
<tr>
<th>$v$</th>
<th>$E_{v+1}^{\text{nonrel}} - E_v^{\text{nonrel}}$</th>
<th>$E_{v+1}^{\text{rel}} - E_v^{\text{rel}}$</th>
<th>Prev. calc. [46]</th>
<th>Exper. [44]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1736.778</td>
<td>1736.759</td>
<td>1736.707</td>
<td>1736.66</td>
</tr>
<tr>
<td>11</td>
<td>1415.162</td>
<td>1415.128</td>
<td>1415.076</td>
<td>1415.07</td>
</tr>
<tr>
<td>12</td>
<td>1049.247</td>
<td>1049.194</td>
<td>1049.139</td>
<td>1049.16</td>
</tr>
<tr>
<td>13</td>
<td>622.088</td>
<td>622.015</td>
<td>621.956</td>
<td>622.02</td>
</tr>
</tbody>
</table>

respectively. The latter difference indicates that our calculations produced essentially identical transition frequencies as those obtained by Wolniewicz. Some small positive differences that appear for the transitions up to $v = 10$ (none of them larger than 0.005 cm$^{-1}$) indicate that our non-BO energies are likely to be slightly less tightly converged than the energies of Wolniewicz. As mentioned, it usually takes more basis functions to obtain the same quality of the results for higher excited states than for the lower states, because of the higher number of nodes in the wave functions of the higher states. In the case of slightly lower accuracy of the calculated energy value for the $v + 1$ state than for the $v$ state, the transition frequency is slightly overestimated. This is the effect to which we attribute the small differences between our and Wolniewicz’s values. However, for the highest three transitions, our transition frequencies are lower than those of Wolniewicz and the difference increases to $-0.010$ cm$^{-1}$ for the highest transition. Whether this is due to lower precision of Wolniewicz’s results for the states at the top of the vibrational spectrum or due to possible artifacts in the nonlinear parameter optimization for highly excited states in our calculations (i.e. when for some reason the energy is better converged for the $v + 1$ state than for the $v$ state) is not immediately clear.

In Table 4.3 we show a comparison between the calculated transition frequencies obtained using the total energies of the vibrational states corrected and uncorrected for the relativistic effects with the experimental frequencies of Dabrowski. Only
the top four transitions are shown in the table. Those are the transitions whose frequencies are likely to be overestimated by the non-BO calculations. After adding the relativistic corrections the agreement between the experimental results and the calculated values improves for all four transitions. The agreement is the best for the top $14 \rightarrow 13$ transition and, as expected, worsens as the vibrational quantum number decreases. For that top transition the non-BO frequency uncorrected for the relativistic effects is 622.088 cm$^{-1}$ and the corrected one is 622.015 cm$^{-1}$ which is very close to the experimental transition of 622.02 cm$^{-1}$. In Table 4.3 we also included the transition frequencies obtained by Wolniewicz using his non-BO energies corrected for electronic relativistic and radiative effects calculated within the BO approximation [46]. As one notices, while for the top two states our and Wolniewicz’s results agree equally well with the experiment, for the next two states Wolniewicz’s results are slightly better. We attribute this to the growing importance of the relativistic magnetic interactions which Wolniewicz included in his calculations and we have not. It should be remembered that the presented comparison is subject to the inaccuracy of the experimental transitions that was mentioned before.

For comparison purpose, we also present our transition frequencies vs those of Wolniewicz [46] for all pure vibrational transitions. This data is shown in table 4.4.

Finally, in Table 4.5 we present the expectation values of the interparticle distances and their squares obtained with 5000 function basis sets. Those include proton–proton, proton–electron, and electron–electron distances. These results show that for the top states the internuclear and interelectronic distances are, as expected, considerably larger than for the bottom states. For those top states the magnetic relativistic corrections should be much smaller than the mass–velocity and Darwin corrections.

To illustrate the nodal structure of the vibrational part of the wave function we included plots of the nucleus–nucleus correlation function for a few vibrational states. These are shown on figure 4.1.
Table 4.4: Relativistically corrected transition frequencies for H$_2$, $E_{v+1}^{\text{rel}} - E_v^{\text{rel}}$ [30], and frequencies obtained by Wolniewicz [46] that include relativistic and radiative corrections. All values are in cm$^{-1}$.

<table>
<thead>
<tr>
<th>$v$</th>
<th>$E_{v+1}^{\text{rel}} - E_v^{\text{rel}}$</th>
<th>Wolniewicz [46]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
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<td>4161.167</td>
</tr>
<tr>
<td>1</td>
<td>3925.904</td>
<td>3925.836</td>
</tr>
<tr>
<td>2</td>
<td>3695.452</td>
<td>3695.389</td>
</tr>
<tr>
<td>3</td>
<td>3468.035</td>
<td>3467.976</td>
</tr>
<tr>
<td>4</td>
<td>3241.622</td>
<td>3241.564</td>
</tr>
<tr>
<td>5</td>
<td>3013.905</td>
<td>3013.851</td>
</tr>
<tr>
<td>6</td>
<td>2782.190</td>
<td>2782.136</td>
</tr>
<tr>
<td>7</td>
<td>2543.228</td>
<td>2543.175</td>
</tr>
<tr>
<td>8</td>
<td>2293.002</td>
<td>2292.950</td>
</tr>
<tr>
<td>9</td>
<td>2026.402</td>
<td>2026.351</td>
</tr>
<tr>
<td>10</td>
<td>1736.759</td>
<td>1736.707</td>
</tr>
<tr>
<td>11</td>
<td>1415.128</td>
<td>1415.076</td>
</tr>
<tr>
<td>12</td>
<td>1049.194</td>
<td>1049.139</td>
</tr>
<tr>
<td>13</td>
<td>622.015</td>
<td>621.956</td>
</tr>
</tbody>
</table>

Table 4.5: Expectation values of the H$_2$ interparticle distances ($r_1 \equiv r_{pp}$, $r_2 \equiv r_{pe}$, $r_{23} \equiv r_{ee}$) obtained with 5000 basis function sets [30]. All values are in a.u.

<table>
<thead>
<tr>
<th>$v$</th>
<th>$\langle r_1 \rangle$</th>
<th>$\langle r_2 \rangle$</th>
<th>$\langle r_{23} \rangle$</th>
<th>$\langle r_1^2 \rangle$</th>
<th>$\langle r_2^2 \rangle$</th>
<th>$\langle r_{23}^2 \rangle$</th>
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</thead>
<tbody>
<tr>
<td>0</td>
<td>1.44874</td>
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<td>2.20133</td>
<td>2.12705</td>
<td>3.14539</td>
<td>5.80533</td>
</tr>
<tr>
<td>1</td>
<td>1.54535</td>
<td>1.62571</td>
<td>2.26584</td>
<td>2.47400</td>
<td>3.36512</td>
<td>6.15743</td>
</tr>
<tr>
<td>2</td>
<td>1.64606</td>
<td>1.67848</td>
<td>2.33448</td>
<td>2.85682</td>
<td>3.60174</td>
<td>6.54189</td>
</tr>
<tr>
<td>3</td>
<td>1.75171</td>
<td>1.73354</td>
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</tr>
<tr>
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<td>1.86342</td>
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<td>2.48828</td>
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</tr>
<tr>
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</tr>
<tr>
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<td>2.67508</td>
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</tr>
<tr>
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<td>6.45252</td>
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<td>10.20725</td>
</tr>
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<td>7.48237</td>
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</tr>
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<td>3.27007</td>
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<td>6.93083</td>
<td>12.72449</td>
</tr>
<tr>
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<td>3.52301</td>
<td>10.56675</td>
<td>7.87601</td>
<td>14.66611</td>
</tr>
<tr>
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<td>3.87464</td>
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<td>9.25452</td>
<td>17.54054</td>
</tr>
<tr>
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<td>2.87265</td>
<td>4.42340</td>
<td>17.67911</td>
<td>11.59453</td>
<td>22.43467</td>
</tr>
<tr>
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<td>5.55825</td>
<td>28.91193</td>
<td>17.33540</td>
<td>34.27670</td>
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</table>
Figure 4.1: Nucleus–nucleus correlation function, $g_1(\xi)$, for $v=0,1,2,5,10,14$ vibrational states of $H_2$. All quantities are in a.u.
4.2 Charge asymmetry in HD$^+$ and HT$^+$ molecular ions

The singly deuterated isotopomer of the H$_2$ cation, HD$^+$, has been used for several decades in model studies of the coupling between the electronic and nuclear motions [47]. In HD$^+$ the lack of a center of symmetry, due to the different nuclear masses, creates a particularly interesting situation that requires a theoretical approach that may differ from those used to describe the parent cation, H$_2^+$, and its symmetric isotopomer, D$_2^+$. The asymmetry of the HD$^+$ system has been investigated both experimentally [48, 49] and theoretically [50, 51, 52]. In recent work Ben–Itzhak et al. [48] studied the dissociation of the electronic ground state of HD$^+$ following ionization of HD by fast proton impact and found the H$^+$ + D(1s) dissociation channel is more likely than the H(1s) + D$^+$ dissociation channel by about 7%. They attributed this asymmetry breakdown to the finite nuclear mass correction to the Born–Oppenheimer (BO) approximation, which makes the 1s$\sigma$ state 3.7 meV lower than the 2p$\sigma$ state at the dissociation limit.

Near the dissociation limit the density of states in the HD$^+$ spectrum increases. If one considers only the ground rotational state manifold (i.e. consider only states with total angular momentum equal to zero), one finds states where the dissociation energy of the system becomes close to the difference between the total energies of the H and D atoms (equal to 29.84 cm$^{-1}$). The D atom is energetically more stable because it has slightly larger reduced mass than H, which makes the electron slightly closer, on average, approach the nucleus resulting in stronger coulombic attraction and a lower energy. In that region the vibrational wave function that corresponds to, say, $v$=20 combined with the ground state electronic wave function that places the electron at the proton, has similar energy as the wave function with the vibrational component corresponding to $v$=21 and with the electronic component localizing the electron at the deuteron. Since such two wave functions have the same symmetry, their mixing can occur. This non–adiabatic coupling must be included in the calculation of the dissociation of HD$^+$ that yields a proton plus a deuterium which is the lowest–energy dissociation product of this system.
In nearly all theoretical calculations of $\text{H}_2^+$ and its isotopes' spectra reported in the literature a body-fixed coordinate system with the origin at the geometric center of the nuclei has been used. For example, in the recent work of Esry and Sadeghpour [51], as well as the works of Moss [50, 52, 53], the starting point was the $\text{H}_2^+$ BO Hamiltonian in prolate spheroidal coordinates (PSC); and electronic wave functions and energies were first obtained as a function of the internuclear distance. Here we demonstrate the capability of the variational method to treat such systems fully non-adiabatically [23]. The very high powers $m_k$ in the pre-exponential multipliers, which were ranged from 0 to 250, allow one to describe very sharp peaks in the ”vibrational” part of the wavefunction.

The effort in the first series of calculations has been focused on generating very accurate variational wave functions and energies for the rotationless vibrational states of the HD$^+$ ion. To achieve the best results in the parameter optimization with the least computational effort, we have recently implemented a hybrid method that combines the gradient–based optimization with the stochastic selection method [19, 20, 21]. The strategy is based on alternating the gradient–based and the stochastic–based optimizations in growing the basis set from a small initial set generated in a gradient–based optimization to the final set. The basis set for each vibrational state was generated in a separate calculation. We used 2000 basis functions for each state except the ground and first excited state where we limited ourselves to 1000–term expansions, as the energies for those states were essentially converged with this number of functions. Also, in additional calculations for the highest excited state ($v=22$), where we studied the convergence of our approach, we used expansions with up to 4000 basis functions.

In table 4.6 we compare our variational energies with the values of Hilico et al. [54]. As one can see, the values agree very well. The agreement is consistently very good for all the states calculated. We should mention that the energies in the Hilico et al. work [54] were obtained with the CODATA 86 mass values while in our calculations we used more recent CODATA 2002 masses [55]. However, as we have determined, the effect of the mass difference does not exceed the uncertainty due to
Table 4.6: Total energies, expectation values of the deuteron–proton distance, \( r_{d-p} \), the deuteron–electron distance, \( r_{d-e} \), and the proton–electron distance, \( r_{p-e} \), and their squares for the vibrational levels of HD\(^+\) at the rotational ground state. All quantities are a.u.

<table>
<thead>
<tr>
<th>( v )</th>
<th>( E, \text{ our calc.} )</th>
<th>( E, \text{ ref. [54]} )</th>
<th>( \langle r_{d-p} \rangle )</th>
<th>( \langle r_{d-e} \rangle )</th>
<th>( \langle r_{p-e} \rangle )</th>
<th>( \langle r_{d-p}^2 \rangle )</th>
<th>( \langle r_{d-e}^2 \rangle )</th>
<th>( \langle r_{p-e}^2 \rangle )</th>
</tr>
</thead>
<tbody>
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<td>-0.5978979686</td>
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<td>1.688</td>
<td>1.688</td>
<td>4.268</td>
<td>3.534</td>
<td>3.537</td>
</tr>
<tr>
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<td>-0.5891818296</td>
<td>2.171</td>
<td>1.750</td>
<td>1.750</td>
<td>4.855</td>
<td>3.839</td>
<td>3.843</td>
</tr>
<tr>
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<td>5.492</td>
<td>4.169</td>
<td>4.173</td>
</tr>
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<td>1.881</td>
<td>6.185</td>
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</tr>
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</tr>
<tr>
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*D atom in the ground state
the basis incompleteness that we have in our calculations. Our calculations, where we used the old CODATA 86 masses, produced energies shifted down by at most $4 \times 10^{-4}$ a.u. in comparison to the energies obtained with the CODATA 2002 masses. The highest shift was obtained for states in the middle of the spectrum with $v$ near 10. For the lower and higher states the difference due to the CODATA 86/CODATA 2002 mass change was progressively smaller.

In the next step the wave functions for all the 23 states were used to calculate the average internuclear distances and the average distances between the nuclei and the electron. Also, averages of the squares of the distances were calculated. The results are shown in table 4.6. As can be expected, the average internuclear distance increases with the rising level of excitation. This increase becomes more prominent at the levels near the dissociation threshold. For example, in going from $v=21$ to $v=22$ the average internuclear distance increases more than two-fold from 12.95 a.u. to 28.62 a.u. In the $v=22$ state the HD$^+$ ion is almost dissociated. These results agree well with the previous calculations of Moss [56]. However, the most striking feature that becomes apparent upon examining the results is a sudden increase of the asymmetry between the deuteron–electron and proton–electron average distances above the $v=20$ excitation level. In levels up to $v=20$ there is some asymmetry of the electron distribution with the $p$–$e$ distance being slightly longer than the $d$–$e$ distance. For example, in the $v=20$ state the $d$–$e$ average distance is 4.569 a.u. and the $p$–$e$ distance is 5.516 a.u. The situation becomes completely different for the $v=21$ state. Here the $p$–$e$ distance of 12.19 a.u. is almost equal to the average value of the internuclear distance but the $d$–$e$ distance becomes much smaller and equals only 2.306 a.u. It is apparent that in this state the electron is essentially localized at the deuteron and the ion becomes highly polarized. An analogous situation also occurs for the $v=22$ state. Here, again, the $p$–$e$ average distance is very close to the internuclear distance while the $d$–$e$ distance is close to what it is in an isolated D atom.

In figure 4.2 we show the nucleus–nucleus correlation function for some vibrational states of HD$^+$ (the pseudoproton density) [24]. As expected, the number
Figure 4.2: Nucleus–nucleus correlation function, $g_1(\xi)$, for $v=0,1,2,10,20,22$ vibrational states of HD$^+$. All quantities are in a.u.
of oscillations on these plots increases with the excitation level. Also, the spatial extent of the pseudoparticle density increases with the excitation. In higher excited states, though the density shows many oscillations, the highest density maximum is still the one closest to the origin of the coordinate system.

The state with $v=22$ is the highest two state near the dissociation threshold. The spatial extent of the density dramatically increases for this state in comparison with the lower states. Also, in these highest two states ("the ionic states"), the last density maximum counting from the origin becomes much more prominent, indicating that in those states the two nuclei spend more time being significantly separated from each other than being close to each other.

In the same manner as we did for HD$^+$, we performed calculations of HT$^+$ molecular ion [25]. Due to a larger mass difference between the nuclei in HT$^+$ than in HD$^+$, one could expect a stronger charge polarization and a larger number of the vibrational states near the dissociation threshold with the “ionic” character. However, the results of our calculations show that this appears not to be the case. Apart from describing the charge asymmetry in HT$^+$, another goal of this work has been to provide high accuracy estimates of the nonrelativistic energies for all rotationless vibrational states of this ion, which have not been calculated before, except for few low lying ones [36, 57].

In our HT$^+$ calculations we used a 1500-term expansion for the ground and first excited states, a 2000-term expansions for $v=2,3$ states, a 2500-term expansions for $v=4–17$ states, a 3000-term expansion for $v=18–20$ states, a 4000-term expansion for $v=21$ state. In the calculations for the two highest excited states ($v=22, 23$), where the charge symmetry breaking is the most significant, we increased the length of the expansion to 5000.

After the wave functions for all 24 ($v=0, \ldots, 23$) states were generated, we also, like in the case of HD$^+$, calculated the expectation values of the internuclear triton–proton distance, $\langle r_{t-p} \rangle$, the triton–electron ($t-e$) distance, $\langle r_{t-e} \rangle$, and the proton–electron ($p-e$) distance, $\langle r_{p-e} \rangle$, for each state. The average values of the squares of the distances were calculated as well. In our calculations, we used the
Table 4.7: Total energies, expectation values of the triton–proton distance, \(r_{t-p}\), the triton–electron distance, \(r_{t-e}\), and the proton–electron distance, \(r_{p-e}\), and their squares for the rotationless bound states of HT\(^+\). All quantities are in atomic units.

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<th>(\langle r_{t-e}\rangle)</th>
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\(^*\) T atom in the ground state.
following values for the nuclear masses: $m_t = 5496.921503m_e$, where $m_e$ stands for the mass of the electron $m_p = 1836.15267261m_e$. These values were taken from CODATA 2002 [55] list of fundamental constants.

As was mentioned above, the entire vibrational spectrum of HT$^+$ had not been accurately computed prior our work. The only energy values we can compare with our numbers are those of Bishop and Chung ($E_{v=0} = -0.5981761344$, $E_{v=1} = -0.5899328131$, $E_{v=2} = -0.5820800248$ a.u.; all obtained with the mass ratios: $m_e/m_p = 0.000544617$, $m_e/m_t = 0.000181920$ [57]) and Frolov ($E_{v=0} = -0.598176134669766232$ a.u.; obtained with $m_p = 1836.152701m_e$, $m_t = 5496.92158m_e$ [36]). The lower effectiveness of Gaussians in describing the cusps is likely to be partially responsible for the difference between our ground state energy and the value reported by Frolov, who used complex exponential basis functions. In order for our ground state energy to become closer to Frolov's result, we would need to increase the precision of real numbers in our calculations from double (15 digits) to quadruple. This would make the optimization less affected by the numerical noise and more effective. There is another source of the discrepancy between Frolov's ground state energy and ours. It is due to the difference in the proton and triton masses (we used the most current ones, which are slightly lighter leading to our ground state energy being slightly higher than Frolov’s). In order to test how much of a difference this would make, we recalculated the energies of all states using the masses given in Frolov’s paper and we found that our result for the ground state shifts down by about $4 \times 10^{-11}$ hartree. The shift increases with the excitation level and reaches a maximum for the states in the middle of the spectrum ($v=11–13$) where it becomes approximately equal to $4 \times 10^{-10}$ hartree. For the highest levels the shift again becomes smaller, by an order of magnitude. This behavior is expected as it is known that the nonadiabatic effects are the most significant in the middle of the vibrational spectrum.

The analysis of the expectation values of the interparticle distances in table 4.7 shows that, while the bond in HT$^+$ in the lowest 22 vibrational states can be described as covalent, in the highest two states it becomes ionic. In those states the
ion becomes a complex of $T + p$. In $v=23$ state the electron becomes entirely localized around the tritium nucleus and almost completely absent at the proton. This strong, purely nonadiabatic effect occurs when the dissociation energy of a vibrationally excited state becomes close to the difference between the total energies of the H and T atoms.

4.3 Calculations of HeH$^+$

The hydrohelium cation HeH$^+$, whose first laboratory observation dates back to 1925 [58], is relevant to astrochemistry [59] since hydrogen and helium are the two most abundant elements in the universe. Apart from works [26, 28], all previous vibrational calculations of HeH$^+$ in the electronic ground $^1\Sigma^+$ state have been based on the Born–Oppenheimer potential energy curve and they were summarized in the work of Bishop and Cheung [60]. Since HeH$^+$ has a relatively large permanent dipole moment, there have been some highly precise measurements of the vibration–rotational and pure rotational gas phase spectra of this system. However, we should add that HeH$^+$ is a system for which only a couple hundred ro–vibrational transitions have been assigned and no pure vibrational transitions have been measured. Thus, this important system is still “a work in progress” both in terms of the experimental and theoretical investigations. In this paper we show how well these investigations are converging in determining the transition energies between the rotationless vibrational levels.

HeH$^+$ has 12 pure vibrational states ($v=0, ..., 11$). We generated wave functions for all 12 states in separate calculations [28]. For each state we used 5400 basis functions (2.22). After that we calculated the mass-velocity and Darwin corrections and added them to the variational energies of the corresponding states. Those values were used to calculate the transition energies. In the calculations we used the following values for the nuclear masses: $m_{\text{He}} = 7294.2995363m_e$ ($^4\text{He}$ isotop), $m_p = 1836.15267261m_e$ taken from [55]. Here, $m_e$ stands for the mass of the electron.

Since no pure vibrational transitions have been measured for HeH$^+$ we cannot
Table 4.8: Total non-BO energies ($E_{\text{non-BO}}$), mass–velocity corrections (MV), Darwin corrections (Drw), $v + 1 \rightarrow v$ vibrational frequencies calculated without ($\Delta E_{\text{non-BO}}$) and with ($\Delta E_{\text{non-BO+rel}}$) inclusion of relativistic corrections, and first three vibrational frequencies extracted from experimental data using two different methods of extrapolation ($\Delta E_{\text{exp}}^a$ and $\Delta E_{\text{exp}}^b$ respectively). The energies and corrections are given in a.u., the frequencies in cm$^{-1}$.

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<tr>
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<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

* Dissociation threshold

make a direct comparison of our numbers with the experimental values. Instead, we used the values extracted from available experimental data based on two types of fitting: (a) fitting the microwave and infrared spectra of four isotope variants of $^4\text{HeH}^+$ to the radial parameters in the Herman-Ogilvie equation (b) fitting the line positions of the separate bands $1 \rightarrow 0$, $2 \rightarrow 1$, and $3 \rightarrow 2$ of $^4\text{HeH}^+$ to the Dunham’s energy formula. The details of this fitting procedures are described in [28] and references therein.

The total and transition energies for all twelve bound vibrational states of $\text{HeH}^+$ with zero total angular momentum obtained in the non-BO calculations are presented in table 4.8. Both nonrelativistic results and results including the relativistic corrections are shown. All transition energies corrected for the relativistic effects are lower than their uncorrected counterparts. The largest shift of $-0.1508$ cm$^{-1}$ due to the relativistic corrections occurs for the $8 \rightarrow 7$ transition. It is clear that
Table 4.9: Expectation values of purely vibrational states of the HeH$^+$ ion obtained with 5400 basis functions: the internuclear distance ($\langle r_1 \rangle$), the distance between the He nucleus and an electron ($\langle r_2 \rangle$), the distance between the proton and an electron ($\langle r_{12} \rangle$), the distance between electrons ($\langle r_{23} \rangle$), and the squares of the distances. All values are in a.u.

<table>
<thead>
<tr>
<th>$v$</th>
<th>$\langle r_1 \rangle$</th>
<th>$\langle r_2 \rangle$</th>
<th>$\langle r_{12} \rangle$</th>
<th>$\langle r_{23} \rangle$</th>
<th>$\langle r_1^2 \rangle$</th>
<th>$\langle r_2^2 \rangle$</th>
<th>$\langle r_{12}^2 \rangle$</th>
<th>$\langle r_{23}^2 \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.5177</td>
<td>0.93557</td>
<td>1.5619</td>
<td>1.4052</td>
<td>2.3283</td>
<td>1.1809</td>
<td>2.7775</td>
<td>2.4107</td>
</tr>
<tr>
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<td>0.94300</td>
<td>1.6718</td>
<td>1.4210</td>
<td>2.7472</td>
<td>1.2093</td>
<td>3.1932</td>
<td>2.4762</td>
</tr>
<tr>
<td>2</td>
<td>1.7650</td>
<td>0.94906</td>
<td>1.7981</td>
<td>1.4346</td>
<td>3.2529</td>
<td>1.2343</td>
<td>3.7006</td>
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</tr>
<tr>
<td>3</td>
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<td>1.9463</td>
<td>1.4455</td>
<td>3.8798</td>
<td>1.2548</td>
<td>4.3363</td>
<td>2.5847</td>
</tr>
<tr>
<td>4</td>
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<td>1.4530</td>
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<td>1.2695</td>
<td>5.1607</td>
<td>2.6229</td>
</tr>
<tr>
<td>5</td>
<td>2.3209</td>
<td>0.95643</td>
<td>2.3504</td>
<td>1.4568</td>
<td>5.7748</td>
<td>1.2769</td>
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<td>2.6462</td>
</tr>
<tr>
<td>6</td>
<td>2.6156</td>
<td>0.95427</td>
<td>2.6483</td>
<td>1.4561</td>
<td>7.3536</td>
<td>1.2751</td>
<td>7.9108</td>
<td>2.6512</td>
</tr>
<tr>
<td>7</td>
<td>3.0353</td>
<td>0.94945</td>
<td>3.0733</td>
<td>1.4506</td>
<td>9.8893</td>
<td>1.2626</td>
<td>10.5211</td>
<td>2.6347</td>
</tr>
<tr>
<td>8</td>
<td>3.7033</td>
<td>0.94242</td>
<td>3.7472</td>
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<td>14.6320</td>
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<td>15.3683</td>
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</tr>
<tr>
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<td>0.93535</td>
<td>4.9652</td>
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<td>25.6070</td>
<td>1.2147</td>
<td>26.4690</td>
<td>2.5538</td>
</tr>
<tr>
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<td>7.4824</td>
<td>0.93123</td>
<td>7.5225</td>
<td>1.4246</td>
<td>59.3200</td>
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<td>60.3040</td>
<td>2.5274</td>
</tr>
<tr>
<td>11</td>
<td>16.043</td>
<td>0.92979</td>
<td>16.066</td>
<td>1.4225</td>
<td>283.88</td>
<td>1.1945</td>
<td>284.97</td>
<td>2.5182</td>
</tr>
</tbody>
</table>

for all transitions the inclusion of relativistic corrections change the frequencies by much more than their respective experimental errors. The comparison between the calculated transition frequencies and the experimental results for the first three transitions is also shown in table 4.8. As mentioned, only for the first two transitions did the experimental results obtained using both estimation methods agree to high precision. For those two transitions the relativistic corrections bring the predicted frequencies noticeably closer to the experimental values. Although adding the relativistic correction to the third transition (3 $\rightarrow$ 2) also improves the result, there is a discrepancy between the two extrapolated experimental values, making this case less reliable.

The averaged interparticle distances are shown in table 4.9. As expected, the average internuclear distance ($\langle r_1 \rangle$) increases with the vibrational excitation. In the ground state this distance is equal to 1.5177 a.u. and increases to 16.043 a.u. for the highest excited state. The distance between an electron and the helium
Figure 4.3: Nucleus–nucleus correlation function, $g_1(\xi)$, for $v=0,1,2,4,10,11$ vibrational states of HeH$^+$. All quantities are in a.u.
nucleus \( \langle r_1 \rangle \) equals 0.93557 a.u. in the ground state first slightly increases with the excitation level, but starting with the \( v=6 \) level it starts to decrease. This trend indicates that the two electrons stay close to the helium nucleus for all vibrational states. In the lowest states, where the average distance between the helium nucleus and the proton is still relatively short, the electron density polarizes somewhat towards the proton. This polarization slightly increases with the excitation level. However, starting with the \( v=6 \) level, the proton becomes so far removed from the helium atom that the electronic polarization starts to decrease and the electrons center around the helium nucleus as they do in an isolated helium atom. The localization of the electrons around the helium nucleus and away from the proton is also apparent in the behavior of the average electron–proton distance \( \langle r_{12} \rangle \). In the ground state this distance is equal to 1.5619 a.u., but increases to 16.066 a.u. for the highest excited state. The latter value is almost equal to the average internuclear distance for that state. The average interelectron distance \( \langle r_{23} \rangle \) is affected to a small extend by the vibrational excitation. This indicates that the electrons do not part from each other due to the interaction with the proton, but they stay bonded to the helium nucleus. Thus, as expected, the HeH\(^+\) ion regardless of the level of the vibrational excitation can be described as a complex of a slightly polarized helium atom and a proton which, as the level of the vibrational excitation increases, becomes increasingly more distant from the helium atom.

In the end of the section we present the plots of nucleus–nucleus correlation function for several vibrational states of HeH\(^+\). They are shown in figure 4.3.

### 4.4 Vibrational spectrum of LiH\(^+\)

So far we have considered molecular systems that contain no more then two electrons. While many highly accurate approaches are restricted to two-electron systems, the variational method with explicitly correlated Gaussians allows consideration of larger molecules. Below we present the results of our calculations on LiH\(^+\) [31]. This system has three electrons and electronic correlations here are significantly
more complicated. The main reason for this is the fact that the wave function of the electrons, more precisely its spacial part, has mixed permutational symmetry (not fully symmetric as in the case of \( \text{H}_2 \)).

The previous calculations of Berriche et al. [61] of the vibrational spectrum in the ground electronic state of the \( \text{LiH}^+ \) system predicted the existence of seven bound vibrational states. Those calculations were done within the Born–Oppenheimer approximations and the electronic energy was determined with a method that utilized an effective core potential. Thus, they can be expected to be significantly less accurate than non-BO variational calculations with the use of explicitly correlated Gaussians. In our calculations we used 5600 basis functions (2.22) for each vibrational state. As always, each state was calculated separately, meaning all nonlinear parameters and powers were optimized for that state.

We start the presentation of the results by showing the convergence of the total energies of the ground and excited vibrational states as the function of the size of the basis set. The number of states whose energies we have managed to converge below the dissociation threshold was six. An attempt made to converge the seventh state below the dissociation threshold failed. With nearly 5000 functions in the basis set the energy was still above the threshold and the convergence pattern did not indicate a realistic possibility of lowering the energy below the threshold.

The convergence patterns of the energies of the six vibrational states are shown on figure 4.4, where, for each state, we plotted the difference between the energy obtained with a particular number of basis functions and the energy obtained with 5600 functions. It is expected that it takes more basis functions to obtain the same quality of the results for higher excited states than for the lower states because of the larger number of radial nodes in the wave functions of the higher states. Figure 4.4 demonstrates this trend very well. The curve corresponding to the ground state \((v = 0)\) is flat, indicating that the energy of this state is already very well converged with 4500 basis functions while the energy of \(v = 5\) state with that many functions is still far from the same degree of convergence.

In table 4.10 we show the values of the total energy we obtained with 3200, 4400,
Figure 4.4: Convergence of the total energy, $E_v$, for $v=0−5$ of LiH$^+$. $K$ is the number of basis functions.

Table 4.10: Non-BO total energies of LiH$^+$ vibrational states obtained with 3200, 4400, and 5600 basis functions. All values are in a.u.

<table>
<thead>
<tr>
<th>$v$</th>
<th>3200</th>
<th>4400</th>
<th>5600</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>−7.78324642</td>
<td>−7.78324679</td>
<td>−7.78324691</td>
</tr>
<tr>
<td>1</td>
<td>−7.78162705</td>
<td>−7.78162820</td>
<td>−7.78162885</td>
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<tr>
<td>2</td>
<td>−7.78043317</td>
<td>−7.78043546</td>
<td>−7.78043619</td>
</tr>
<tr>
<td>3</td>
<td>−7.77965589</td>
<td>−7.77966016</td>
<td>−7.77966140</td>
</tr>
<tr>
<td>4</td>
<td>−7.77924363</td>
<td>−7.77925034</td>
<td>−7.77925191</td>
</tr>
<tr>
<td>5</td>
<td>−7.77903864</td>
<td>−7.77908792</td>
<td>−7.77909093</td>
</tr>
</tbody>
</table>
Table 4.11: Transition frequencies for LiH\(^+\) vibrational states obtained with 3200, 3600, 4000, 4400, 4800, 5200, and 5600 function basis for each state versus the frequencies of Berriche et al. [61]. All values are in cm\(^{-1}\).

<table>
<thead>
<tr>
<th>(v' \rightarrow v)</th>
<th>3200</th>
<th>3600</th>
<th>4000</th>
<th>4400</th>
<th>4800</th>
<th>5200</th>
<th>5600</th>
<th>ref. [61]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(\rightarrow 0)</td>
<td>355.411</td>
<td>355.338</td>
<td>355.279</td>
<td>355.241</td>
<td>355.197</td>
<td>355.158</td>
<td>355.125</td>
<td>357.43</td>
</tr>
<tr>
<td>2(\rightarrow 1)</td>
<td>262.027</td>
<td>261.901</td>
<td>261.828</td>
<td>261.775</td>
<td>261.757</td>
<td>261.754</td>
<td>261.757</td>
<td>265.61</td>
</tr>
<tr>
<td>3(\rightarrow 2)</td>
<td>170.592</td>
<td>170.364</td>
<td>170.240</td>
<td>170.160</td>
<td>170.107</td>
<td>170.070</td>
<td>170.047</td>
<td>172.96</td>
</tr>
<tr>
<td>4(\rightarrow 3)</td>
<td>90.480</td>
<td>90.176</td>
<td>90.018</td>
<td>89.945</td>
<td>89.911</td>
<td>89.889</td>
<td>89.874</td>
<td>92.20</td>
</tr>
<tr>
<td>5(\rightarrow 4)</td>
<td>44.990</td>
<td>37.691</td>
<td>36.121</td>
<td>35.647</td>
<td>35.460</td>
<td>35.367</td>
<td>35.331</td>
<td>37.45</td>
</tr>
<tr>
<td>6(\rightarrow 5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>9.22</td>
</tr>
</tbody>
</table>

and 5600 basis functions for each of the vibrational state [31].

In the case of slightly lower accuracy of the calculated energy value for the \(v + 1\) state than for the \(v\) state the transition energies, \(E_{v+1} - E_v\), are usually slightly overestimated. Thus, our calculated transition energies shown in table 4.11 should provide upper bounds to the exact results. In table 4.11 we not only include the transition energies obtained with the largest basis set of 5600 functions, but we also show how the energies converge with the number of basis functions. The convergence pattern allows us to estimate the accuracy of our calculations. It is safe to state that this accuracy is of the order of 0.1 cm\(^{-1}\).

For comparison purpose we also included in table 4.11 transition energies obtained by Berriche et al. [61]. All their energies are higher than ours by 2-4 cm\(^{-1}\). To what extent this is an effect of not assuming the Born–Oppenheimer approximation in our calculations and/or to what extent this results from inaccuracies of the potential energy curve calculated by Berriche et al., it is, at this point, difficult to say.

In Table 4.12 we present the expectation values of the interparticle distances and their squares for the six bound vibrational states obtained with 5,600 basis functions for each state. Those include lithium nucleus–proton \(\langle r_{\text{Li}-p}\rangle\), lithium nucleus–electron \(\langle r_{\text{Li}-e}\rangle\), proton–electron \(\langle r_{\text{p}-e}\rangle\), and electron–electron \(\langle r_{\text{e}-e}\rangle\) distances. The results show that the internuclear distance increases, as expected, with the vibra-
Table 4.12: Mean interparticle distances of LiH$^+$ and mean squares of the interparticle
distances calculated with 5600 basis functions for each state [31]. Here, $r_{Li-p} \equiv r_1$,
$r_{Li-e} \equiv r_2$, $r_{p-e} \equiv r_12$, and $r_{e-e} \equiv r_{23}$. All values are in a.u.

<table>
<thead>
<tr>
<th>$v$</th>
<th>$\langle r_{Li-p} \rangle$</th>
<th>$\langle r_{Li-e} \rangle$</th>
<th>$\langle r_{p-e} \rangle$</th>
<th>$\langle r_{e-e} \rangle$</th>
<th>$\langle r^2_{Li-p} \rangle$</th>
<th>$\langle r^2_{Li-e} \rangle$</th>
<th>$\langle r^2_{p-e} \rangle$</th>
<th>$\langle r^2_{e-e} \rangle$</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>4.82188</td>
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<td>3.74209</td>
<td>3.53807</td>
<td>23.8518</td>
<td>8.63460</td>
<td>17.2254</td>
<td>17.2837</td>
</tr>
<tr>
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<td>3.30029</td>
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<td>55.0501</td>
</tr>
<tr>
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<td>8.99011</td>
<td>8.80871</td>
<td>170.743</td>
<td>57.9530</td>
<td>115.130</td>
<td>115.918</td>
</tr>
</tbody>
</table>

It also can be noticed that the average value of the proton–electron
distance parallels the average value of the electron–electron distance. This indicates
that, when the vibrational excitation moves the nuclei further apart, two electrons
stay with the Li nucleus and one moves away with the proton. Thus, at the limit
LiH$^+$ dissociates into Li$^+$ and H.

The increase of the internuclear distance with the vibrational excitation is the
result of the radial function describing the system becoming increasingly more diffuse
and oscillating more. This effect is shown in figure 4.4 where the nucleus–nucleus
correlation function, which is the same as the density of pseudoparticle 1 (i.e. pseudoproton), is plotted for all vibrational states of LiH$^+$.

### 4.5 LiH and LiD electron affinity

The determination of electron affinities (EAs) is one of the most serious problems in
quantum chemistry. While the Hartree-Fock electron affinity can be easily evaluated,
most anions turn out to be unbound at this level of theory. Thus, the correlation
effects are extremely crucial to evaluate EAs. At this point, lithium hydride and
lithium hydride anion make up a very good benchmark system because they are
still small enough yet exhibit features of more complicated systems. Four and five
electrons respectively give rise to higher order correlation effects that are not possible
in H$_2$. 

Figure 4.5: Nucleus–nucleus correlation function, $g_1(\xi)$, for all vibrational pure states of LiH$^+$. All quantities are in a.u.
The theoretical interest in the LiH\(^-\) has increased since the electron affinity of LiH and its deuterated counterpart, LiD, were measured with the use of the photoelectron spectroscopy by Bowen and coworkers \cite{62}. The adiabatic electron affinities of \(^{7}\text{LiH}\) and \(^{7}\text{LiD}\) determined in that experiment were 0.342\(\pm\)0.012 eV for the former and 0.337\(\pm\)0.012 eV for the latter system. The appearance of these data posed a challenge for theory to reproduce those values in rigorous calculations based on the first principles. Since the two systems are small, it has been particularly interesting to see if the experimental EAs can be reproduced in calculations where the BO approximation is not assumed \cite{21}.

Since the time Bowen’s et al. paper was published, the theory based on the BO approximation, except for one very recent multi-reference configuration interaction (MRCI) calculation by Chang et al., \cite{63} has been unable to produce a value of the LiH adiabatic electron affinity that falls within the experimental uncertainty bracket. More than that, in many works where authors managed to obtain an EA that was relatively close to the experimentally determined one, the success was often due to fortuitous cancellation of errors in the total energies of LiH and LiH\(^-\) rather than the accuracy achieved in calculations. This inability seems somewhat odd, since there is nothing particularly unusual about and fundamentally difficult to describe in the LiH\(^-\)/LiH system. Since the LiH molecule is a polar system (Li\(\delta^+\)–H\(\delta^-\)) an excess electron in the process of attachment localizes on the electropositive alkali atom in a nonbonding orbital of the neutral molecule.

We would like to mention that one should not expect the non-adiabatic effects to play a noticeable role in the LiH and LiD electron affinity calculations. However, by applying the non-BO approach we can directly determine the total energies of the anion and the neutral system in one-step calculations, and we do not need to resort to calculating the electronic potential energy curves for the anion and the neutral first and using them for calculating their nuclear vibration energies in the next step, as it is done in the BO approach. Thus, using the non-BO method we not only make the calculation free of any artifacts that may result from the two-step procedure used in the BO approximation, but we also obtain total and relative energies that, if the
basis sets become more complete, approach the true non-relativistic limits of those quantities, free of any approximations.

In comparison with such systems as HD\(^+\), H\(_2\), and HeH\(^+\), more sophisticated LiH and LiH\(^-\) represent a significantly more challenging case from the point of view of computational demands, even if we restrict themselves with the consideration of the ground state only. The total number of particles is 6 in the case of LiH and 7 in the case of LiH\(^-\), which means that effectively we deal with 15 and 18-dimensional problem respectively. Considering that the number of permutations in the Young operator also increases as the number of identical particles increases (this number is 24 for LiH and 120 for LiH\(^-\)), the amount of computational work required for performing sound calculations rises by a factor of several orders of magnitude. To attempt such calculations at present time one has to gain an access to large-scale parallel computer systems. However, with advances in computer hardware, this kind of calculations may soon become quite ordinary and even routine.

The results of our calculations for the energy are shown in table 4.13. In table 4.14 we show the values of the LiH and LiD electron affinities calculated as the difference of the energies of the anion and the neutral system for all lengths of the basis set for which the total energies are reported. A question can be raised whether it is appropriate to use the total energies obtained with the same length of the basis set for LiH\(^-\) and LiH (or LiD\(^-\) and LiD) in the electron affinity calculation. Since LiH\(^-\) has one more electron than LiH, it should require more basis functions for LiH\(^-\) than for LiH to achieve a similar level of accuracy of the results. This is indeed showing in the convergence of the results presented in table 4.13. Certainly the 3600-term energy for LiH is better converged than the 3600-term energy for LiH\(^-\). It should be mentioned that the LiH and LiD variational energies obtained in work [21] are the lowest non-BO ground-state energies ever obtained for these systems. It is significantly lower than the previous non-BO value of \(-8.06615576\) hartree, which was also obtained in our group [18]. The same is true about the LiH\(^-\) and LiD\(^-\) energies, though in this case the final values are not as tightly converged as the energies for LiH and LiD. Also, work [21], to date, is the only one where a
Table 4.13: Non-BO variational ground state energies of the LiH−, LiH, LiD−, and LiD molecules obtained with different basis sets [21]. All energies are in atomic units.

<table>
<thead>
<tr>
<th>basis size</th>
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<th>LiH−</th>
<th>LiD−</th>
</tr>
</thead>
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<td>−8.07778128</td>
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</tr>
<tr>
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<td>−8.0794715</td>
<td>−8.07875507</td>
</tr>
<tr>
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<td>−8.06636491</td>
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<td>−8.0807991</td>
<td>−8.07888651</td>
</tr>
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<td>−8.06734116</td>
<td>−8.0830536</td>
<td>−8.07912238</td>
</tr>
<tr>
<td>2000</td>
<td>−8.06640408</td>
<td>−8.06735333</td>
<td>−8.0837566</td>
<td>−8.07919877</td>
</tr>
<tr>
<td>2200</td>
<td>−8.06641099</td>
<td>−8.06736128</td>
<td>−8.0842711</td>
<td>−8.07925549</td>
</tr>
<tr>
<td>2400</td>
<td>−8.06641554</td>
<td>−8.06736613</td>
<td>−8.0846014</td>
<td>−8.07929081</td>
</tr>
<tr>
<td>2600</td>
<td>−8.06642068</td>
<td>−8.06737208</td>
<td>−8.0848753</td>
<td>−8.07931985</td>
</tr>
<tr>
<td>2800</td>
<td>−8.06642353</td>
<td>−8.06737514</td>
<td>−8.0851089</td>
<td>−8.07934370</td>
</tr>
<tr>
<td>3000</td>
<td>−8.06642581</td>
<td>−8.06737749</td>
<td>−8.0852933</td>
<td>−8.07936248</td>
</tr>
<tr>
<td>3200</td>
<td>−8.06642787</td>
<td>−8.06737962</td>
<td>−8.0854406</td>
<td>−8.07937759</td>
</tr>
<tr>
<td>3400</td>
<td>−8.06642941</td>
<td>−8.06738123</td>
<td>−8.0855805</td>
<td>−8.07939162</td>
</tr>
<tr>
<td>3600</td>
<td>−8.06643070</td>
<td>−8.06738251</td>
<td>−8.0856887</td>
<td>−8.07940445</td>
</tr>
</tbody>
</table>

The variational, non-BO calculation of the ground-state of a five-electron system such as LiH− or LiD− has been attempted. Since LiH (LiD) energy at a particular basis set size is better converged than the LiH− (LiD−) energy, the calculated electron affinity is always lower than the result would be in the limit of the complete basis set. Thus, by calculating the EA at the basis set with the same size for the anion and for neutral system and by incrementally increasing the size of the basis, we could monitor the EA convergence and be sure that all the EA values we calculated including the final value (this being the 3600-term result) are lower bounds to the true EA.

As shown in table 4.14 our best results for LiH and LiD electron affinities obtained with the 3600-term expansions of the wave functions for LiH−/LiH and LiD−/LiD are 0.33030 and 0.32713 eV, respectively. Even though, as stated, both values represent lower bounds to the true EAs, they both are within the uncertainty brackets of the experimental results of 0.342±0.012 eV (LiH) and 0.337±0.012 eV (LiD) obtained by Bowen and coworkers [62].
Table 4.14: Convergence of the electron affinities of LiH and LiD (in eV) in terms of the number of the basis functions [21] and the corresponding experimental values of Sarkas et al. [62].

<table>
<thead>
<tr>
<th>basis size</th>
<th>LiH</th>
<th>LiD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>0.31186</td>
<td>0.30869</td>
</tr>
<tr>
<td>1200</td>
<td>0.31572</td>
<td>0.31218</td>
</tr>
<tr>
<td>1400</td>
<td>0.31878</td>
<td>0.31512</td>
</tr>
<tr>
<td>1600</td>
<td>0.32213</td>
<td>0.31856</td>
</tr>
<tr>
<td>1800</td>
<td>0.32410</td>
<td>0.32056</td>
</tr>
<tr>
<td>2000</td>
<td>0.32576</td>
<td>0.32233</td>
</tr>
<tr>
<td>2200</td>
<td>0.32698</td>
<td>0.32366</td>
</tr>
<tr>
<td>2400</td>
<td>0.32775</td>
<td>0.32449</td>
</tr>
<tr>
<td>2600</td>
<td>0.32836</td>
<td>0.32512</td>
</tr>
<tr>
<td>2800</td>
<td>0.32891</td>
<td>0.32568</td>
</tr>
<tr>
<td>3000</td>
<td>0.32935</td>
<td>0.32613</td>
</tr>
<tr>
<td>3200</td>
<td>0.32970</td>
<td>0.32648</td>
</tr>
<tr>
<td>3400</td>
<td>0.33004</td>
<td>0.32682</td>
</tr>
<tr>
<td>3600</td>
<td>0.33030</td>
<td>0.32713</td>
</tr>
<tr>
<td>experiment</td>
<td>0.342 ± 0.012</td>
<td>0.337 ± 0.012</td>
</tr>
</tbody>
</table>
Table 4.15: Expectation values of the internuclear distance, $r_1 \equiv r_{LiH}$, and its square (in a.u.) for LiH, LiD, LiH$^-$, and LiD$^-$, calculated with the 3600 basis functions \[21\].

<table>
<thead>
<tr>
<th>system</th>
<th>$\langle r_1 \rangle$</th>
<th>$\langle r_1^2 \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiH$^-$</td>
<td>3.21471</td>
<td>10.3939</td>
</tr>
<tr>
<td>LiH</td>
<td>3.06105</td>
<td>9.41973</td>
</tr>
<tr>
<td>LiD$^-$</td>
<td>3.19974</td>
<td>10.2836</td>
</tr>
<tr>
<td>LiD</td>
<td>3.04913</td>
<td>9.33435</td>
</tr>
</tbody>
</table>

Finally, table 4.15 shows the expectation values of the internuclear distance and its square for LiH, LiD, LiH$^-$, and LiD$^-$. Here we see trends that can be easily understood considering that the attachment of an excess electron weakens slightly the Li–H bond and that increasing the mass of H by switching to D results in making the vibrational component of the total wave function more localized resulting in a slight contraction of the average length of the bond. This contraction is very similar in going from LiH and LiD and from LiH$^-$ to LiD$^-$.  

### 4.6 Molecules containing positron: $e^+LiH$

During the last several years much advance has been made concerning the study of bound states of the positron with small systems. The ability of various atoms, ions, and molecules to bind a positron is now well established and represent a popular subject of research. However, most of the calculations performed were done on atomic systems (or those containing just one particle significantly heavier than the positron). For example, there has been considerable interest to the positronium hydride, HPs ($p^+e^+e^-e^-$) and its isotopomers (see \[64, 65, 66\] and references therein). Molecular systems containing positron have been mainly treated with the use of Quantum Monte Carlo \[67, 68\] or variational method \[69, 70, 71\] assuming BO approximation. An attempt of calculating $e^+LiH$ was made in paper \[72\], where authors used simple gaussians (without premultipliers). However, the convergence of the total energy turned out to be very slow while the basis size was not large, which resulted in relatively low accuracy of the calculations.
Table 4.16: Total non-Born–Oppenheimer energies of HPs, LiH, and $e^+\text{LiH}$ as a function of basis size [20]. All values are in a.u.

<table>
<thead>
<tr>
<th>basis size</th>
<th>HPs</th>
<th>LiH</th>
<th>$e^+\text{LiH}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>$-0.7888705040$</td>
<td>$-8.066278419$</td>
<td>$-8.103075429$</td>
</tr>
<tr>
<td>1000</td>
<td>$-0.7888705983$</td>
<td>$-8.066320545$</td>
<td>$-8.103572816$</td>
</tr>
<tr>
<td>1200</td>
<td>$-0.7888706398$</td>
<td>$-8.066344535$</td>
<td>$-8.103905788$</td>
</tr>
<tr>
<td>1400</td>
<td>$-0.7888706611$</td>
<td>$-8.066364905$</td>
<td>$-8.104113213$</td>
</tr>
<tr>
<td>1600</td>
<td>$-0.7888706790$</td>
<td>$-8.066382950$</td>
<td>$-8.104256550$</td>
</tr>
<tr>
<td>1800</td>
<td>$-0.7888706877$</td>
<td>$-8.066394978$</td>
<td>$-8.104372009$</td>
</tr>
<tr>
<td>2000</td>
<td>$-0.7888706940$</td>
<td>$-8.066404077$</td>
<td>$-8.104478249$</td>
</tr>
<tr>
<td>2200</td>
<td>$-0.7888706984$</td>
<td>$-8.066410987$</td>
<td>$-8.104543434$</td>
</tr>
<tr>
<td>2400</td>
<td>$-0.7888707014$</td>
<td>$-8.066415542$</td>
<td>$-8.104598552$</td>
</tr>
<tr>
<td>2600</td>
<td>$-0.7888707036$</td>
<td>$-8.066420678$</td>
<td>$-8.104645276$</td>
</tr>
<tr>
<td>2800</td>
<td>$-0.7888707057$</td>
<td>$-8.066423527$</td>
<td>$-8.104683502$</td>
</tr>
<tr>
<td>3000</td>
<td>$-0.7888707062$</td>
<td>$-8.066425806$</td>
<td>$-8.104713922$</td>
</tr>
<tr>
<td>3200</td>
<td>$-0.7888707066$</td>
<td>$-8.066427866$</td>
<td>$-8.104739913$</td>
</tr>
</tbody>
</table>

In work [20] we raised the question of whether one can use basis functions (2.22) in non-BO quantum mechanical calculations of molecular diatomic systems containing positrons and whether those functions are capable of providing a proper representation for the positron–nucleus and positron–electron correlation effects in a diatomic system. $e^+\text{LiH}$ was choses as a target system. Along with $e^+\text{LiH}$ we also performed the calculations of HPs and Li$^+$ as the total energies of these systems are needed for determining the dissociation energy.

The convergence of the energy values for HPs, LiH, and $e^+\text{LiH}$ in terms of the number of basis functions is shown in table 4.16. In the case of $e^+\text{LiH}$, as well as for LiH case, the powers $m_k$ in (2.22) were selected from the interval 0–200. Although the positronium hydride wave function can be obtained with very high precision even without using powers of the hydrogen–positron distance in the pre–exponential factors in the basis functions, we did included some functions with small preexponential powers ranged from 0 to 10 to ensure better numerical stability in the calculations.

From the lowest energy values shown in table 4.16 one can determine that the
positron detachment energy of $e^+\text{LiH}$, $\text{PDE}=E(e^+\text{LiH})-E(\text{LiH})$, is 0.038312 a.u. The lowest-energy fragmentation of $e^+\text{LiH}$ corresponds to dissociation of the system into HPs + Li$^+$. To calculate the dissociation energy, $\text{DE}=E(e^+\text{LiH})-E(\text{Li}^+)-E(\text{HPs})$, one needs to determine the total energy of the Li$^+$ ion. Since the non-BO calculation of this quantity is very simple, rather than taking it from the literature, we recalculated it using our method. A 400-term expansion was sufficient to obtain highly accurate result of $-7.279321518$ a.u., where, we believe, all the significant figures shown are exact.

Given the values of the HPs and Li$^+$ energies calculated in this work in addition to that of $e^+\text{LiH}$, our dissociation energy is 0.036548 a.u. This value qualitatively agrees with the value of 0.0382(2) a.u. obtained in the BO calculations by Mella and coworkers [67] using the Quantum Monte Carlo method. It also agrees with the BO result of 0.036936 obtained by Strasburger [71] with the use of explicitly correlated Gaussians and the variational method.

The lowest variational energy upper-bound for the Born–Oppenheimer LiH ground state energy to date is $-8.070538$ a.u. [73]. Assuming that the energies of Li and H with infinitely heavy nuclei are $-7.4780603$ [74] and $-0.5$ a.u. respectively, one obtains the infinite mass dissociation energy of LiH of $-0.0924777$ a.u. The finite mass energy of LiH can be estimated by subtracting this number from the sum of the finite mass energies of Li and H atoms and by adding to the result the zero-point LiH energy. Using the finite mass energy of Li of $-7.4774519$ a.u., which one can calculate by using the expansion from the paper of Yan and Drake [74], the corresponding value for the H atom of $-0.4997278$ a.u., and the zero-point LiH energy of 0.0031981 a.u. (see Ref. [75]) we obtain the LiH ground state energy corrected for the finite nuclear masses equal to $-8.066459$ a.u. The use of experimentally determined zero-point energy of $-0.0031799$ [76] shifts this value to $-8.066478$ a.u. The difference between this value and our non-BO result of $-8.066427866$ a.u. is larger than the estimated sum of their inaccuracies. Although, perhaps, this may partially be attributed to relatively low accuracy of the zero-point energy, it is clear that the nonadiabatic effect of the coupled electron–nuclear motion must play a role
Table 4.17: Expectation values of the Li–H internuclear distance, its square, and electron–positron contact densities evaluated with 3200 basis functions [20]. All quantities are in a.u.

<table>
<thead>
<tr>
<th>system</th>
<th>( \langle r_{\text{LiH}} \rangle )</th>
<th>( \langle r_{\text{LiH}}^2 \rangle )</th>
<th>( \langle \delta(r_{e^-e^+}) \rangle )</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPs</td>
<td>–</td>
<td>–</td>
<td>2.44855 \times 10^{-2}</td>
</tr>
<tr>
<td>LiH</td>
<td>3.06105</td>
<td>9.41977</td>
<td>–</td>
</tr>
<tr>
<td>(e^+)LiH</td>
<td>3.44470</td>
<td>11.9397</td>
<td>7.08879 \times 10^{-3}</td>
</tr>
</tbody>
</table>

In the difference.

In table 4.17 we present expectation values of the internuclear distance and its square for LiH and \(e^+\)LiH as well as the electron–positron contact densities for HPs and \(e^+\)LiH evaluated with the largest basis set of 3200 basis functions obtained in the calculations. It should be noted that the mean internuclear distance of LiH calculated here is slightly higher than the known value, 3.015 a.u., of the equilibrium nuclear distance, i.e. the distance where the potential energy curve reaches its minimum. This is, obviously, an expected result since larger distances contribute more to the mean distance when one averages the internuclear distance over the “vibrational” part of the wave function, even if a purely Born–Oppenheimer calculation is carried out, and, hence, the mean distance is always larger than the distance corresponding the peak of the vibrational component of the wave function (minimum of the potential energy curve). This discrepancy becomes more and more noticeable as the nuclear masses decrease. For \(e^+\)LiH our \(r_{\text{LiH}} \ (\equiv r_1)\) mean distance of 3.445 a.u. agrees well with the equilibrium internuclear separation of 3.348 a.u. obtained by Strasburger [71] in the Born–Oppenheimer calculations.

An important characteristic of positronic systems relevant to the experiment is their lifetimes. The expectation value of the electron–positron contact density allows to evaluate the two-photon annihilation rate for a positronic system using the expression

\[
\Gamma_{2\gamma} = n \frac{\pi \alpha^4 c}{a_0} \langle \delta(r_{e^-e^+}) \rangle, \tag{4.1}
\]

where \(\alpha\) is the fine structure constant, \(a_0\) is the Bohr radius, \(c\) is the velocity of
light, and \( n \) denotes the number of electron–positron pairs in the system (2 and 4 in the case of HPs and \( e^+\text{LiH} \) respectively). The two-photon annihilation rates we obtained with 3200 basis functions are: \( 2.4716 \times 10^{9} \text{sec}^{-1} \) for HPs, \( 1.4311 \times 10^{9} \text{sec}^{-1} \) for \( e^+\text{LiH} \). This indicates that a positron attached to LiH survives much longer than in the HPs system. The HPs annihilation rate can be compared with the result of Yan and Ho obtained in a finite-mass calculation using Hylleraas coordinates [77] (HPs) and with the explicitly correlated Gaussian calculation [65] performed for \( \infty\text{HPs} \) (HPs with infinitely heavy proton) which both yielded the value of \( 2.4722 \times 10^{9} \text{sec}^{-1} \).

In the case of \( e^+\text{LiH} \) we can make a comparison with the Born–Oppenheimer Quantum Monte Carlo result of Mella and co-workers [68], which yielded \( 1.49 \times 10^{9} \text{sec}^{-1} \) (the vibrationally averaged result) and with the BO explicitly correlated Gaussian result of Strasburger [71] where the value of \( 1.375 \times 10^{9} \text{sec}^{-1} \) was obtained at the \( e^+\text{LiH} \) equilibrium distance of \( R = 3.348 \text{ a.u.} \)

4.7 First purely vibrational transition in LiH

One of the most spectacular achievements of the quantum mechanical calculations of molecular systems that occurred is the early stage of the development of the field (late sixties – early seventies) was the very accurate calculations of the ground and excited states of the \( \text{H}_2 \) molecule performed by Kolos, Wolniewicz and collaborators (see [78] and references therein). Those calculations helped revise the experimental data and correct some inaccuracies of the initial measurements. Since that time there have been numerous instances of works where the theoretical calculations combined with experimental measurements have helped elucidate various phenomena that occur in molecular systems. However, the precision achieved for diatomic systems with two electrons, such as that in the Kolos and Wolniewicz calculations, has not been achieved for system with three, four and more electrons. Below we show that due to the development of the very accurate variational non-BO methods concerning stationary states of diatomic systems and the new more precise spectral measurements, it is possible now to extend the theoretical–experimental interaction
similar to that for \( H_2 \) to a diatomic molecular system with four electrons – the LiH molecule [27].

The calculations presented here concern only the ground state pure vibrational transition (the 0\(\rightarrow\)1 transition) in the LiH molecule. Since the energy of that transition is not directly available from the experiment, an extrapolation procedure (described briefly in [27]) was used to estimate that energy. The calculations of the ground and first excited pure vibration states of LiH have lasted for over a year and they have certainly been one of the most time and resource-consuming pieces of work that we have ever performed.

The wave functions of both vibrational states were generated in separate calculations. To achieve high accuracy we used 7200 basis functions for each state [27]. Later we additionally optimized the basis sets and extended them to 7500 functions.

After the wave functions were generated and total nonrelativistic energies were computed, we evaluated the expectation values of the interparticle distances and the squares of the distances. The values of the nuclear masses used in the calculations were \( m_{\text{Li}} = 12786.3933 m_e \) (\(^7\text{Li}\)), \( m_p = 1836.15267261 m_e \) with \( m_e \) being the mass of the electron.

The first series of the results we show concerns the convergence of the total non-BO energies of the ground and the first excited state as the number of the basis functions increases. These results are presented in table 4.18. In the table we also show the convergence of the 0\(\rightarrow\)1 transition energy and its comparison with the value derived from the experiment using the procedure described in [27].

Since it can be exacted that within the same number of basis functions the energy of the ground state is better converged than the energy of the first excited state (due to the more complicated structure of the excited state wave function requiring more basis functions to reach comparable precision as for the ground state), the transition energy calculated as the difference of total energies of the two states should provide, in practice, an upper bound to the result one should get at the complete basis set limit. Inspection of the transition energies presented in table 4.18 shows that this is indeed the case. The calculated transition energy decreases as the number of
Table 4.18: Convergence of the total energies of the \(v = 0\) and \(v = 1\) states and the \(1 \leftrightarrow 0\) transition energy for LiH.

<table>
<thead>
<tr>
<th>basis size</th>
<th>(E_{v=0}) (a.u.)</th>
<th>(E_{v=1}) (a.u.)</th>
<th>(\Delta E) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>-8.06632054</td>
<td>-8.05992010</td>
<td>1404.735</td>
</tr>
<tr>
<td>2000</td>
<td>-8.06640408</td>
<td>-8.06014697</td>
<td>1373.277</td>
</tr>
<tr>
<td>3000</td>
<td>-8.06642580</td>
<td>-8.06019856</td>
<td>1366.720</td>
</tr>
<tr>
<td>4000</td>
<td>-8.06643237</td>
<td>-8.06021956</td>
<td>1363.555</td>
</tr>
<tr>
<td>5000</td>
<td>-8.06643445</td>
<td>-8.06022786</td>
<td>1362.189</td>
</tr>
<tr>
<td>6000</td>
<td>-8.06643587</td>
<td>-8.06023300</td>
<td>1361.372</td>
</tr>
<tr>
<td>7000</td>
<td>-8.06643680</td>
<td>-8.06023636</td>
<td>1360.838</td>
</tr>
<tr>
<td>7500</td>
<td>-8.06643736</td>
<td>-8.06023831</td>
<td>1360.534</td>
</tr>
<tr>
<td>Experiment</td>
<td></td>
<td></td>
<td>1359.7083(19)</td>
</tr>
</tbody>
</table>

The availability of the wave functions describing the rotationless internal motion of LiH in the ground and excited states allowed the calculation of the expectation values of the interparticle distances and their squares. Relativistic mass–velocity and Darwin corrections were also computed. They are presented in table 4.19. As expected, the average internuclear distance \(\langle r_1 \rangle\) increases with the vibrational excitation. In the ground state this distance is equal to 3.06104 a.u. and increases to 3.15501 a.u. for the first excited state. The averaged electron–nucleus distances, as well as the inter–electron distance, also increase when the system is excited from the ground to the first vibrational state.

The inclusion of Mass-velocity and Darwin corrections changes the transition
Table 4.19: Expectation values for \( v=0 \) and \( v=1 \) rotationless states of LiH computed with 7500 basis functions.

<table>
<thead>
<tr>
<th>quantity</th>
<th>( v = 0 )</th>
<th>( v = 1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \langle r_{\text{Li-H}} \rangle )</td>
<td>3.06104</td>
<td>3.15501</td>
</tr>
<tr>
<td>( \langle r_{\text{Li-e}} \rangle )</td>
<td>1.97193</td>
<td>2.00701</td>
</tr>
<tr>
<td>( \langle r_{\text{H-e}} \rangle )</td>
<td>2.56510</td>
<td>2.62428</td>
</tr>
<tr>
<td>( \langle r_{e-e} \rangle )</td>
<td>2.95594</td>
<td>3.00879</td>
</tr>
<tr>
<td>( \langle r_{\text{Li-H}}^2 \rangle )</td>
<td>9.41971</td>
<td>10.1047</td>
</tr>
<tr>
<td>( \langle r_{\text{Li-e}}^2 \rangle )</td>
<td>6.58572</td>
<td>6.86654</td>
</tr>
<tr>
<td>( \langle r_{\text{H-e}}^2 \rangle )</td>
<td>7.74517</td>
<td>8.17109</td>
</tr>
<tr>
<td>( \langle r_{e-e}^2 \rangle )</td>
<td>10.9660</td>
<td>11.3947</td>
</tr>
<tr>
<td>MV correction</td>
<td>(-4.2084\times10^{-3} )</td>
<td>(-4.2054\times10^{-3} )</td>
</tr>
<tr>
<td>Darwin correction</td>
<td>(3.4032\times10^{-3} )</td>
<td>(3.4006\times10^{-3} )</td>
</tr>
</tbody>
</table>

energy from 1360.534 cm\(^{-1}\) to 1360.617 cm\(^{-1}\), which takes us somewhat further from the experiment, 1359.7083(19) cm\(^{-1}\). On this basis we may conclude that, unlike in the HeH\(^+\) case, other kinds of relativistic corrections (such as orbit–orbit) play an important role in LiH and must be included to improve the agreement between the theory and experiment.

Finally, in figure 4.7 we show the nucleus–nucleus correlation functions for \( v=0 \) and \( v=1 \) states of LiH.

Although only two vibrational states were calculated, the procedure would not be any different for higher excited states. Due to the increasing number of the radial nodes in terms of the \( r_1 \) coordinate in those state it is certain that more basis functions will be needed, but the accuracy of the calculations should not be any lower than the accuracy of the results presented above. As mentioned, at the time of the calculations our computer resources did not allow to undertake studies of higher excited states of LiH and an access would be needed to a computer two orders of magnitude faster than what we had available to us to carry out such work.
Figure 4.6: Nucleus–nucleus correlation function, \( g_1(\xi) \), for the ground (solid line) and first vibrationally excited (dashed line) states of LiH. All quantities are in a.u.

4.8 Test calculations with complex Gaussians

In this section we present some results for a few test systems obtained with complex Gaussian basis functions (2.23). The development of the approach that utilizes complex Gaussians is still at the beginning stage. Thus, only preliminary results are available at this time. The main goal of the calculations presented below was the verification of the analytic expressions and studying general properties of the complex Gaussian basis set relevant to numerical calculations. Therefore, we did not consider systems that contain more than 5 particles, and did not run calculations with large basis sets as this would have been a rather time consuming task. The work on writing an efficient parallel computer code, suitable for large scale calculations with complex Gaussians, is currently underway and the results of such calculations will be published as they become available.

As a three-particle example for our tests we picked HD\(^+\) molecular ion, whose vibrational levels for the case of zero total angular momentum were accurately computed in work [23]. Using complex Gaussians we carried out calculations of the
Table 4.20: HD$^+$ total energies (in a.u.) at the ground rotational state computed with different basis sets.

<table>
<thead>
<tr>
<th>basis size</th>
<th>$v=0$</th>
<th>$v=1$</th>
<th>$v=2$</th>
<th>$v=3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>complex Gaussians</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>$-0.5964479$</td>
<td>$-0.5845906$</td>
<td>$-0.5692322$</td>
<td>$-0.5562954$</td>
</tr>
<tr>
<td>50</td>
<td>$-0.5977843$</td>
<td>$-0.5886749$</td>
<td>$-0.5797404$</td>
<td>$-0.5708290$</td>
</tr>
<tr>
<td>100</td>
<td>$-0.5978855$</td>
<td>$-0.5891622$</td>
<td>$-0.5808242$</td>
<td>$-0.5729303$</td>
</tr>
<tr>
<td>Gaussians with premultipliers</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>$-0.5977373$</td>
<td>$-0.5878143$</td>
<td>$-0.5782370$</td>
<td>$-0.5648660$</td>
</tr>
<tr>
<td>50</td>
<td>$-0.5978904$</td>
<td>$-0.5891295$</td>
<td>$-0.5807355$</td>
<td>$-0.5726804$</td>
</tr>
<tr>
<td>100</td>
<td>$-0.5978967$</td>
<td>$-0.5891762$</td>
<td>$-0.5808721$</td>
<td>$-0.5729620$</td>
</tr>
<tr>
<td>real Gaussians</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>$-0.5927791$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>$-0.5959859$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>$-0.5975521$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>exact, reference [23]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$-0.5978980$</td>
<td>$-0.5891818$</td>
<td>$-0.5809037$</td>
<td>$-0.5730505$</td>
</tr>
</tbody>
</table>

In the calculations we applied a simultaneous optimization of all nonlinear variational parameters utilizing the analytic gradient. The basis sets used in these calculations consisted of 25, 50, and 100 functions. For demonstrational purpose we also performed analogous calculations using real Gaussian basis functions with premultipliers in the form of even powers of the internuclear distance 2.22.

The results of the calculations are presented in table 4.20. Even though small basis sets were used, they clearly show that complex Gaussians can be applied not only in ground state calculations of diatomics, but also in calculations of vibrationally excited states. The convergence rate in the case of complex Gaussians appears to be somewhat slower than the one of Gaussians with premultipliers in the form of powers of the internuclear distance. This fact was not surprising since the degree of “localization” of the Gaussians with premultipliers around their maxima can be very well adjusted by increasing the value of the power, which makes those func-
Table 4.21: Ground state energy of Li atom (in a.u.) calculated with complex and real Gaussian basis functions.

<table>
<thead>
<tr>
<th>basis size</th>
<th>real Gaussians</th>
<th>complex Gaussians</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>−7.474121</td>
<td>−7.476282</td>
</tr>
<tr>
<td>50</td>
<td>−7.476469</td>
<td>−7.477239</td>
</tr>
<tr>
<td>100</td>
<td>−7.476931</td>
<td>−7.477409</td>
</tr>
<tr>
<td>exact*</td>
<td>−7.477452</td>
<td></td>
</tr>
</tbody>
</table>

*Computed using data from reference [74] with $^7$Li nucleus mass.

We also made an attempt to carry out the same calculations with real Gaussians (without premultipliers), that have been very popular in atomic calculations. These basis functions performed quite poorly, as expected. In the table we show numbers only for the ground state ($v=0$) since the calculations for vibrationally excited states simply could not be completed due to severe numerical instabilities. It is a known fact that in calculations of systems where particle masses differ significantly and the heavy particles have the same sign charges (like in the molecular case) real Gaussians have a strong tendency to become nearly linear dependent (upon optimization of their nonlinear parameters) and this causes instabilities that are difficult to overcome. These instabilities also appeared in the ground state calculations with real Gaussians. But there they were not that severe, which made it possible for us to perform optimization and obtain energy values that are stable in the significant figures presented.

The second example we considered was a four-particle system – Li atom. Again, in order to see how well complex Gaussians performed we carried out analogous calculations with real Gaussians. The results are shown in table 4.21. As expected, complex Gaussians demonstrate better convergence than the real ones, which is mainly due to the fact that these basis functions have more nonlinear parameters, and, hence, are more flexible.

We would like to note that energies in tables 4.21 and 4.20 give only a general idea about the convergence rates with different basis functions. These numbers
should not be considered the best possible values that can be obtained. In fact, they can vary quite noticeably depending on such factors as the initial guess for the nonlinear parameters, optimization algorithm employed, and scaling of the variables. The process of the optimization of the nonlinear variational parameters for basis sets larger than few tens is rather complex. As the number of functions increases, the energy hypersurface becomes more and more complicated and, generally, there is never a hope to find the absolutely lowest minimum. Nonetheless, it is possible in most situations to obtain fairly consistent results in terms of the energy vs basis functions used.

The most interesting example we present in this section concerns the calculations of the ground state of H$_2$D$^+$ ion. Three-atomic case has been a big challenge in precise non-BO variational studies because of complicated nuclei density distribution that is very difficult to describe very accurately using commonly used basis functions. Even though the ground states of such systems can be, in principle, studied using gaussians with shifted centers (2.21), going to excited states is problematic because the latter basis functions do not possess certain angular momentum. We hope that the development of the approach that utilizes complex Gaussians will eventually make the calculations of vibrationally exited states of three-atomic systems possible.

In table 4.22 we present the total energies of H$_2$D$^+$ obtained with 200 and 300 complex Gaussians. For comparison purpose, we also included in this table the data for shifted Gaussians from work [79].

Upon looking at this table one can notice that the result obtained with 200 complex Gaussian basis functions is relatively poor compared to the results produced by shifted Gaussians with similar basis sizes. However, the situation improved significantly when the basis was expanded to 300 functions. If this tendency is kept upon further increase of the number of basis functions, then complex Gaussians may reveal better performance than the Gaussians with shifted centers.

We should mention that the calculations with a few hundreds of complex Gaussians are time demanding and require an order of magnitude more computational
Table 4.22: Total energy of the ground state of H$_2$D$^+$ computed with complex Gaussian basis functions.

<table>
<thead>
<tr>
<th>basis size</th>
<th>$E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>complex Gaussians</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>$-1.31745$</td>
</tr>
<tr>
<td>300</td>
<td>$-1.31997$</td>
</tr>
<tr>
<td>shifted Gaussians [79]</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>$-1.31699$</td>
</tr>
<tr>
<td>118</td>
<td>$-1.31884$</td>
</tr>
<tr>
<td>247</td>
<td>$-1.32051$</td>
</tr>
<tr>
<td>493</td>
<td>$-1.32161$</td>
</tr>
<tr>
<td>951</td>
<td>$-1.32221$</td>
</tr>
<tr>
<td>1400</td>
<td>$-1.32270$</td>
</tr>
</tbody>
</table>

resources than those that deal with any kind of real Gaussians (mainly because of complex arithmetic). Thus, the implementation of effective algorithms for calculating matrix elements and solving generalized eigenvalue problem on parallel computer systems, as well as the development of new, more efficient schemes for optimization of nonlinear parameters becomes extremely important in order to fully utilize the strenghts of the complex Gaussian basis set.
CONCLUSIONS AND FUTURE DIRECTIONS

In this dissertation we described our work on development and implementation of methods for quantum mechanical calculations of molecular systems without assuming Born-Oppenheimer approximation regarding the separability of the electronic and nuclear motions. The centerpiece of the development has been the use of different types of explicitly correlated Gaussian basis functions. The use of such functions has been very successful in many applications that deal with bound states of few-electron molecular systems. These basis functions allow to obtain highly accurate solutions of the nonrelativistic Schrödinger equation and estimate relativistic corrections. Many results obtained through this development, which are presented in chapter 4, are the most accurate ones to date.

The motivation for developing the nonadiabatic approach to describe states of molecules stems from realization that in order to reach the accuracy of modern experimental measurements in quantum chemical calculations, one must to account for the coupling between the motions of electrons and nuclei and for the relativistic effects. With the development of such methods fundamental notions of molecular quantum mechanics can be explored.

At present time our effort concentrates on the extension of the highly accurate non-BO approach to the system containing three and more nuclei. Our aim is to match the accuracy we have been getting for the diatomic systems. This is a very challenging task and requires very large amount of work to be done. But we hope that, once completed, it will open to us the possibility highly vibrationally excited, charged, and neutral clusters of hydrogen and its isotopomers, as well as other light elements.

Besides considering systems with more than two nuclei, it is of great practical interest to study states of diatomic molecules with higher than zero total angular momenta. This would allow a direct comparison of the theoretical transitional frequencies with the experimental ones.
Another development that represents a significant interest is the calculation of relativistic and QED corrections for small molecular systems. So far we have been able to implement a method of calculating the mass-velocity and Darwin corrections. Even though these two are the largest ones in absolute values, other corrections, such as the one due to spin–orbit interaction are of the same order of magnitude and need be taken into account.
REFERENCES


[45] L. Wolniewicz, (private communication); 9, 78, 79


