Equivalent Quantum Approach to Nuclei and Electrons in Molecules

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Contents

I. Introduction

The majority of chemical systems and chemical processes can be theoretically described within the Born-Oppenheimer (BO) approximation[1,2] which assumes that nuclear and electronic motions can be separated. With this separation, the states of the electrons can be determined from the electronic Schroedinger equation, which depends only parametrically on the nuclear positions through the potential energy operator. As a result the calculations of dynamical processes in molecules can be divided into two parts: the electronic problem is solved for fixed positions of atomic nuclei, and then the nuclear dynamics on a given predetermined electronic potential surface or surfaces, in the case of near degenerate electronic states, is considered. The most important consequence of the above approximation is the potential-energy surface (PES) concept, which provides a conceptual as well as a computational base for molecular physics and chemistry. Separation of the nuclear and electronic degrees of freedom has had significant impact and has greatly simplified the theoretical view of the properties of molecules. The molecular properties can be rationalized by considering the dynamics on a single electronic PES, in most cases the PES of the ground state. Phenomena and processes such as internal rotational barriers, dissociation, molecular dynamics, molecular scattering, transitions to other electronic states, and infrared and microwave spectroscopy have simple and intuitive interpretations based on the PES concept.[3]

Theoretical determination of PES's for ground and excited states has been one of the primary objectives of quantum chemistry. One of the most remarkable developments in this area in the last two decades has been the theory of analytical derivatives.[4] This theory involves calculation of derivatives of the BO potential energy with respect to the nuclear coordinates or magnitudes of external fields. Besides the use of analytical derivatives in characterizing the local curvature of PES's, they are required for calculation of electronic and magnetic properties (energy derivatives with respect to applied external field) as well as in calculations of forces and force constants.

Theoretical justification of the BO approximation is not a trivial matter. One should mention here a study presented by Wooley[5-8] and Wooley and Sutcliffe.[6] They draw attention to the fact that the BO approximation cannot be justified in any simple way in a completely nonclassical theory. This is related to the most essential philosophical concepts of quantum mechanics.

An increasing amount of evidence has been accumulated indicating that a theoretical description of certain chemical and physical phenomena cannot be accomplished by assuming separation of the nuclear and electronic degrees of freedom. There are several cases which are known to violate the BO approximation due to a strong correlation of the motions of all particles involved in the system. For these kinds of systems the BO approximation is usually invalid from the beginning. Examples of such types of behavior of particular interest to molecular physicist can be found in the following systems: (1) excited dipole-bound anionic states of polar molecules, (2) single and double Rydberg states, (3) muonic molecules, and (4) electron-positronium systems.

One of the most important problems in modern quantum chemistry is to reach "spectroscopic" accuracy in quantum mechanical calculations, (*i.e.*, error less than 1 order of 1 μhartree). Modern experimental techniques such as gas-phase ion-beam spectroscopy reach accuracy on the order of 0.001 cm^{-1}.[9,10] Such accuracy is rather difficult to accomplish in quantum mechanical calculations even for such small one-electron systems as H_2^+ or HD^+. To theoretically reproduce the experimental results with equal accuracy it is necessary to consider corrections beyond the exact solution of the nonrelativistic electronic Schroedinger equation. Naturally, the desire to computationally reproduce experimental accuracy has generated interest in the nonadiabatic approach to molecules. Most work in this area has been done for three-particle systems and the majority of the relevant theory has been developed for such restricted cases.

The conventional nonadiabatic theoretical approach to three-particle systems has been based on the sep-

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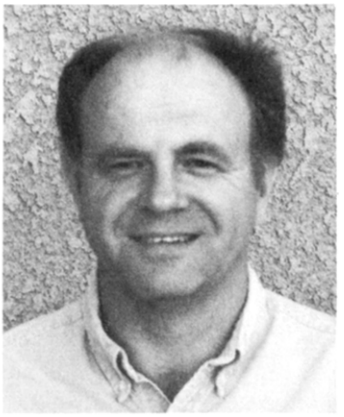

Ludwik Adamowicz was born in Poland in 1950. He received his M.Sc. degree in theoretical chemistry from Warsaw University in 1973 working under the supervision of Profesor W. Kolos. He received his Ph.D. degree in 1977 from the Institute of Chemical Physics, the Polish Academy of Sciences, where he worked under the direction of Prof. A. J. Sadlej on utilizing explicitly correlated Gaussian functions and many-body perturbation theory to study electron correlation effects in molecules. Before and after obtaining the doctoral degree he worked in the Calorimetry Department at the Institute of Chemical Physics, the Polish Academy of Sciences, under the direction of Prof. W. Zielenkiewicz. In 1980 he joined Prof. E. A. McCullough at Utah State University as a postdoctoral fellow and worked on the development of the MCSCF numerical method for diatomic systems. In 1983 he moved to the Quantum Theory Project, University of Florida, to work with Prof. R. J. Bartlett on a number of projects related to development and implementation of the couple-cluster method. In 1987 he assumed a faculty position at the University of Arizona. His current research includes development and implementation of nonadiabatic methodology for many-body systems, multireference coupled-cluster method, application studies on molecular anions, nucleic acid bases, van der Waals complexes, and related systems.

aration of the internal and external degrees of freedom, *i.e.*, transformation to the center-of-mass (CM) frame. This has been achieved by coordinate transformation. The choice of the coordinate system is not unique, and a number of possibilities have been considered by different authors. Some of them will be discussed in more detail in the next section (section II). The coordinate transformation to the CM frame facilitates separation of the Schroedinger equation into a set of uncoupled equations, one representing the translational motion of the CM, and the other representing the internal motion of the system. The next step following coordinate transformation consists of variational solution of the internal eigenvalue problem with a trial function which possesses appropriate rotational properties. "Appropriate" rotational properties include the requirement that the variational wave function be an eigenfunction of the $\hat{J}^2$ operator and its $\hat{J}_z$ component for the whole system defined with respect to CM. Some attempts have been made to solve the nonadiabatic problem for an arbitrary system following the strategy outlined above; however, practical realizations have been so far restricted to the three body problem.

A slightly different approach has been taken for diatomic molecules. The derivation of the nonadiabatic equations for diatomic molecules involves two steps. The first step is exactly the same as for the three-particle case. The second step is the separation of the rotational coordinates. This separation is accomplished by transforming from the space-fixed axes to a set of rotating molecule-fixed axes. The internal molecular Hamiltonian, which results after removal of the translational and rotational coordinates, contains a number of cross-terms, such as mass polarization terms and terms coupling different rotation eigenfunctions. The cross-terms which appear in the internal Hamiltonian couple the momenta of the particles which leads to a certain type of correlation of their internal motions. These terms are also responsible for the fact that the total linear momentum and the total angular momentum of the molecule remain constant. In practice further simplifications are made and some coupling terms are neglected in the internal Hamiltonian.

Taking into account the complications resulting from the transformation of the coordinate system as well as difficulties to preserve appropriate permutational property of the wave function expressed in terms of internal coordinates, we have recently been advancing an alternate approach where the separation of the CM motion was achieved not through transformation of the coordinate system, but in an effective way by introducing an additional term into the variational functional representing the kinetic energy of the CM motion. Our preliminary nonadiabatic calculations on some three- and four-particle systems have shown that with this new method a similar level of accuracy could be reached as in the conventional methods based on explicit separation of the CM coordinates from the internal coordinates. The advantage of this new method is that one can easily extend this approach to systems with more particles due to the use of the conventional Cartesian coordinate system and explicitly correlated Gaussian functions in constructing the many-body nonadiabatic wave function. Also the required permutational symmetry of the wave function can be easily achieved in this approach.

In this review we will discuss the approaches taken in the past to theoretically describe nonadiabatic many-particle systems. In particular we will emphasize the

attempts reaching beyond the three-particle case and the problems related to the separation of CM. In the context of the results achieved by others we will present our contributions to the field.

II. Born–Oppenheimer Approximation and Its Validity

The Born–Oppenheimer (BO) approximation formulated in 1927[1] and a modification, the adiabatic approximation formulated in 1954,[2] also known as the Born–Huang (BH) expansion, constitute two of the most fundamental notions in the development of the theory of molecular structure and solid-state physics. The approximations assume separation of nuclear and electronic motions. The BO approximation and adiabatic approximation have been studied both analytically and numerically. The literature concerning this subject is rather extensive, but some relevant review articles exist, for example those written by Ballhausen and Hansen,[11] Köppel, Domcke, and Cederbaum,[12] as well as Kresin and Lester.[13]

Before we proceed to nonadiabatic theory, for clarity of the presentation let us first summarize some results concerning the BO approximation. This approximation can be theoretically derived with the use of perturbation theory, where the perturbation is the kinetic energy operator for the nuclear motion. It is commonly accepted that the BO approximation should be based on the fact that the mass of the electron is small in comparison to the mass of the nuclei. In the perturbation approach to the BO separation of the electronic and nuclear motion, the perturbation parameter is assumed to be $\kappa = (m_e/M)^{1/4}$,[1,13,15] where M is the mass of largest nuclei. The total Hamiltonian separates as

$$\hat{H} = \hat{H}_0 + \kappa^4 \hat{T}_N \tag{2.1}$$

The choice of the perturbation parameter is not unique, since only the magnitude of κ is taken into consideration in this expansion rather than its accurate value. This parameter can be also taken as the ratio $\kappa = (m_e/\mu)^{1/4}$, where μ denotes the reduced mass of the nuclei.[36]

A different derivation of the BO separation of electronic and nuclear motion was presented by Essen.[14] The main idea of Essen's work was to introduce coordinates of collective and individual motions instead of nuclear and electronic coordinates. He demonstrated that the size of m_e/M is irrelevant and that the nature of the Coulomb interactions between particles involved in a system rather than their relative masses is responsible for the separation. Practical realization of some aspects presented in Essen's paper was proposed by Monkhorst[15] in conjunction with the coupled-cluster method. Monkhorst reexamined the BO approximation and the BH expansion with explicit separation of the CM, which was omitted in the original paper of Born and Oppenheimer. An interesting study of the BO approximation for $(m/M)^{1/2} \rightarrow 0$ was carried out by Grelland.[16] In another recent study, which supports the original Essen's idea, Witkowski[17] demonstrated that a more appropriate separation parameter should be the difference in energy levels rather than the mass ratio.

The simplest way of deriving the BO approximation results from the BH expansion, called also the adiabatic approximation. In the adiabatic approximation[2] the total Hamiltonian,

$$\hat{H} = \hat{H}_0 + \hat{T}_N \tag{2.2}$$

is separated into the Hamiltonian for the clamped nuclei approximation, $\hat{H}_0$, and the kinetic energy operator for the nuclei, $\hat{T}_N$. The solution for the electronic problem,

$$\hat{H}_0 \psi_n(\mathbf{r};\mathbf{R}) = \epsilon_n(\mathbf{R})\psi_n(\mathbf{r};\mathbf{R}) \tag{2.3}$$

only parametrically dependent on the nuclear positions, is assumed to be known. In the above equation $\mathbf{r}$ and $\mathbf{R}$ denote the sets of the electronic and nuclear coordinates respectively. The eigenvalue problem with the Hamiltonian of eq 2.2

$$(\hat{T}_N + \hat{H}_0)\Psi(\mathbf{r},\mathbf{R}) = E\Psi(\mathbf{r},\mathbf{R}) \tag{2.4}$$

can be obtained in terms of the following BH expansion

$$\Psi(\mathbf{r},\mathbf{R}) = \sum_n \chi_n(\mathbf{R})\psi_n(\mathbf{r};\mathbf{R}) \tag{2.5}$$

which leads to the following set of equations

$$[\hat{T}_N + \epsilon_n(\mathbf{R}) - E]\chi_n(\mathbf{R}) = \sum_m \hat{\Lambda}_{nm}\chi_m(\mathbf{R}) \tag{2.6}$$

The nonadiabatic operator $\hat{\Lambda}_{nm}$ is given by

$$\hat{\Lambda}_{nm} = -\int d\mathbf{r}\, \psi_n^*[\hat{T}_N,\psi_m] \tag{2.7}$$

where $[\hat{T}_N,\psi_m]$ denotes the commutator. An approximation of eq 2.6 can be created by neglecting the nonadiabatic operators on the right-hand side. This leads to the result

$$[\hat{T}_N + \epsilon_n(\mathbf{R}) - E]\chi_n(\mathbf{R}) = 0 \tag{2.8}$$

which constitutes the BO approximation.

The nonadiabatic coupling operator has the following interpretation: the diagonal part represents the correction to the potential energy resulting from the coupling between the electronic and nuclear motions within the same electronic state, the off-diagonal part represents the same effect but occurring with transition to different electronic states. It is well known that neglecting such terms can be invalid for some cases. One of such cases occurs when electronic and vibrational levels are close together or cross each other. This may lead to behavior known as the Jahn–Teller, Renner, or Hertzbeg–Teller effects and is commonly called multistate vibronic coupling.[12] In order to theoretically describe a system which exhibits this effect, one usually expands the wave function as a product of the electronic and nuclear wave functions, and then solves the vibronic equation. Usually, only a few electronic states need to be taken into consideration in this approach. The above short review of the BO and BH approximations clearly shows why the BH expansion is the preferred method to treat systems with vibronic coupling. The coupling matrix elements can be usually easily calculated numerically with the use of the procedure developed to calculate gradients and Hessian on PES.

Much more difficult from the theoretical point of view are cases when the Born–Oppenheimer approximation is invalid from the beginning, *i.e.*, when the coupling matrix elements $\Lambda_{nm}(\mathbf{R})$ are large for more extended ranges of the nuclear separation and large number of discrete and continuum electronic states.

Such types of behavior can be found, for example, for some exotic systems containing mesons or other light particles and in certain nonrigid molecules such as H_5^+. In such cases a BH expansion slowly converges, or even diverges. The variational rather than perturbational approach is more appropriate for such cases. The application of the nonadiabatic variational approach leads to a wave function where all particles involved in the system are treated equivalently and are delocalized in the space. Correlation of the motions of particles is most effectively achieved by including explicitly the interparticle distances in the variational wave function. We devote the remainder of this review to describe the approaches taken in this area.

III. Nonadiabatic Approach to Molecules

In the next few subsections we would like to briefly review the nonadiabatic approaches made for (A) three-particle systems and (B) diatomic molecules, and in the final subsection (C) we emphasize attempts taken toward theoretical characterization of systems with more than three particles. Before we demonstrate appropriate methodology let us discuss steps that need to be taken to theoretically describe a system composed of number of nuclei and electrons interacting via Coulombic forces. A collection of N particles is labeled in the laboratory-fixed frame as $\mathbf{r}_i$ (i = 1,...,N) with masses M_i and charges Q_i. In a neutral system the sum of all charges is equal to zero. In the laboratory-fixed frame the total nonrelativistic Hamiltonian has the form

$$H_{\text{tot}} = \frac{1}{2}\sum_{i=1}^{N}\frac{\nabla_i^2}{M_i} + \sum_{i=1}^{N-1}\sum_{j>i}^{N}\frac{Q_iQ_j}{r_{ij}} \tag{3.1}$$

According to the first principles of quantum mechanics there three sets of operations, under which the above Hamiltonian remains invariant.[88] These operations are as follows:

(a) All uniform translations, $\mathbf{r}'_i = \mathbf{r}_i + \mathbf{a}$.

(b) All orthogonal transformations, $\mathbf{r}'_i = \mathbf{R}\mathbf{r}_i$, $\mathbf{R}^T\mathbf{R} = 1$, where $\mathbf{R}$ is an orthogonal matrix such that det $\mathbf{R}$ = 1 or −1.

(c) All permutations of identical particles $\mathbf{r}_i \rightarrow \mathbf{r}_j$, if $M_i = M_j$, $Q_i = Q_j$.

For a system of N particles it is always possible to separate the CM motion. This procedure is called setting up a space-fixed coordinate system (or a CM coordinate system). For convenience let us consider following linear transformation

$$(\mathbf{R}_{\text{CM}},\rho_1,...,\rho_{N-1})^{\text{T}} = \mathbf{U}(\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_N)^{\text{T}} \tag{3.2}$$

where $\mathbf{U}$ is $N \times N$ transformation matrix, while $\mathbf{R}_{CM}$ represents vector of the CM motion

$$\mathbf{R}_{\text{CM}} = \frac{1}{m_0}\sum_{i=1}^{N} m_i\mathbf{r}_i \tag{3.3}$$

with

$$m_0 = \sum_{i=1}^{N} m_i \tag{3.4}$$

The transformation matrix $\mathbf{U}$ has the following structure: elements of the first row are $U_{1i} = M_i/m_0$, where m_0 is given by eq 3.4. It is required that internal coordinates should be translationally invariant. As a consequence

$$\sum_{i=1}^{N} U_{ji} = 0 \ (j = 2,3,...,N) \tag{3.5}$$

for all $(N-1)$ rows. Following arguments presented by Sutcliffe,[88] coordinates $(\rho_1,...,\rho_{N-1})$ are independent if the inverse transformation

$$(\mathbf{r}_1,\mathbf{r}_2,...\mathbf{r}_N)^{\text{T}} = \mathbf{U}^{-1}(\mathbf{R}_{\text{CM}},\rho_1,...\rho_{N-1})^{\text{T}} \tag{3.6}$$

exists. Additionally, on the basis of the structure of the last equation one can chose that

$$(\mathbf{U}^{-1})_{i1} = 1 \qquad (i = 1,2,...,N) \tag{3.7}$$

while the inverse requirement on the reminder of $\mathbf{U}^{-1}$ implies that

$$\sum_{i=1}^{N}(\mathbf{U}^{-1})_{ij}m_i = 0 \qquad (j = 2,...,N) \tag{3.8}$$

On the basis of the above relations, transformation to the new coordinates becomes

$$H = -\frac{1}{2m_0}\nabla^2_{\mathbf{R}_{\text{CM}}} - \sum_{i,j=1}^{N-1}\mu_{i_j}^{-1}\nabla_i\nabla_j + \frac{1}{2}\sum_i\sum_j\frac{Q_iQ_j}{f_{ij}(\rho)} \tag{3.9}$$

where

$$\mu_{ij}^{-1} = \sum_{k=1}^{N} U_{ik}U_{jk} \qquad (i,j = 1,...,N-1) \tag{3.10}$$

with

$$f_{ij}(\rho) = [\sum_{\alpha=x,y,z}(\sum_{k=1}^{N-1}[(\mathbf{U}^{-1})_{jk} - (\mathbf{U}^{-1})_{ik}]\rho_{ak})]^{1/2} \tag{3.11}$$

and the CM motion can be separated off. The above separation of coordinates is quite general. One can notice, however, that after separation some additional terms are present in the internal Hamiltonian. The mathematical forms of the additional terms depend on the form of matrix $\mathbf{U}$. It should be mention, that choice of the transformation matrix is not unique. In the next subsections particular realizations of above methodology will be discussed.

A. Three-Particle Systems

The system of three particles with masses (M_1, M_2, M_3) and the charges (Q_1, Q_2, Q_3) with Coulombic interactions between particles is described by the following nonrelativistic Hamiltonian:

$$H_{\text{tot}} = \frac{P_1^2}{2M_1} + \frac{P_2^2}{2M_2} + \frac{P_3^2}{2M_3} + \frac{Q_1Q_2}{r_{12}} + \frac{Q_1Q_3}{r_{13}} + \frac{Q2Q_3}{r_{23}} \tag{3.12}$$

In the above formula $\mathbf{P}_i$ denotes the momentum vector of the ith particle. To separate internal motion from external motion, the following transformations are used.[19,20,22,25]

$$\mathbf{R}_{\text{CM}} = \frac{1}{m_0}(M_1\mathbf{r}_1 + M_2\mathbf{r}_2 + M_3\mathbf{r}_3) \tag{3.13}$$

$$\mathbf{p}_0 = \mathbf{P}_1 + \mathbf{P}_2 + \mathbf{P}_3 \qquad m_0 = M_1 + M_2 + M_3 \tag{3.14}$$

$$\rho_1 = \mathbf{r}_2 - \mathbf{r}_1 \quad \mathbf{p}_1 = \mathbf{P}_2 - \frac{M_2}{m_0}\mathbf{p}_0 \quad \mu_1 = \frac{M_1 M_2}{M_1 + M_2} \tag{3.15}$$

$$\rho_2 = \mathbf{r}_3 - \mathbf{r}_1 \quad \mathbf{p}_2 = \mathbf{P}_3 - \frac{M_3}{m_0}\mathbf{p}_0 \quad \mu_2 = \frac{M_1 M_3}{M_1 + M_3} \tag{3.16}$$

which is particular realization of the transformation discussed previously. After such transformations the Hamiltonian becomes $H_{tot} = T_{CM} + H_{int}$, where

$$T_{CM} = \frac{p_0^2}{2m_0} \tag{3.17}$$

represents the translational energy of the whole system, and

$$H_{int} = \frac{p_1^2}{2\mu_1} + \frac{p_2^2}{2\mu_2} + \frac{\mathbf{p}_1 \cdot \mathbf{p}_2}{M_1} + \frac{Q_1 Q_2}{|\rho_1|} + \frac{Q_1 Q_3}{|\rho_2|} + \frac{Q_2 Q_3}{|\rho_2 - \rho_1|} \tag{3.18}$$

The eigenfunctions of T_{CM} are the plane waves $\exp(ik \cdot r_0)$ with corresponding eigenvalues of $k_0/2m_0$.

By solving the eigenvalue problem $H_{int}\Psi_{int} = E_{int}\Psi_{int}$, one can determine the internal states of the system. Such classical systems as H^-,[27,32] electron–positron system Ps^- $(e^-e^+e^-)$,[18,22,24,33] muonic molecules,[18,19,28,29,31,32,33] and the H_2^+ molecule and its isotopes[19,21,26] were studied with this approach. The internal Hamiltonian represents the total energy of two fictitious particles with masses μ_1 and μ_2 which move in the Coulomb potential of a particle with charge Q_1 located at the origin of the coordinate system. The cross term $\mathbf{p}_1 \cdot \mathbf{p}_2/M_1$, which is proportional to $\nabla_i \cdot \nabla_j$, represents so-called "mass polarization" which results from the nonorthogonality of the new coordinates. Instead of the nonorthogonal transformation one can use an orthogonal one[36] which, however, leads to a more complicated expression for the interaction part of the Hamiltonian. It should be mentioned that the choice of the coordinates given by eqs 3.13 and 3.14 is not unique. Many different coordinates have been proposed to treat the three-particle problem. The most popular coordinates used for such calculations have been the Jacobi and mass-scaled Jacobi coordinates[29–31] and the hyperspherical coordinates.[23]

Following Poshusta's[22] nomenclature, each stationary state of the total Hamiltonian, H_{tot}, can be labeled by $n(k,J,M,\alpha)$, where n counts the energy levels from the bottom of the (k,J,M,α) symmetry manifold. The above symbols have the following interpretations: translational symmetry preserves conservation of the linear momentum which is indicated by k; rotational symmetry about the CM leads to conservation of the angular momentum which is indicated by J and M (J and M represent the fact that the variational wave function is an eigenfunction of the square of the angular momentum operator and its z component); the last term, α, represents the permutational properties of the wave function.

In the variational approach to solving the internal eigenvalue problem, the choice of an appropriate trial wave function represents a difficult problem. One can expect that the most appropriate guess for the internal variational wave function should explicitly depend on interparticle distances since motions of all particles are correlated due to the Coulombic interaction and due to the conservation of the total angular momentum. There are different varieties of such functions. In the majority of three-particle applications the Hylleraas functions were used.[18,24,27,28,32,33] These functions correctly describe the Coulomb singularities and reproduce the cusp behavior of the wave function related to particle collisions. Another type of function used in calculations has been Gaussian functions[22,25,29] which less properly reflect the nature of the Coulombic singularities but are much easier in computational implementation. The choice of the variational functions will be discussed in detail in the next section.

Higher rotational nonadiabatic states can be calculated by using variational wave functions with appropriate rotational symmetries corresponding to the irreducible representation of rotation groups in the three-dimension space. (This can be accomplished with the use of Wigner rotational matrices.) The rotation properties of three-particle nonadiabatic wave functions have been recently extensively studied for muonic molecules in conjunction with muon-catalyzed fusion.[34]

Finally, one should mention that the extremely high level of accuracy that has been achieved in the last few years in nonadiabatic calculations as well as in experimental measurements on three-particle systems has already allowed testing of the limits of the Schroedinger nonrelativistic quantum mechanics.[35,43]

B. Diatomic Molecules

The nonadiabatic study for diatomic molecules has been mostly restricted to the H_2 molecule and its isotopic counterparts. The nonadiabatic results are well documented in articles presented by Kolos and Wolniewicz,[36] Peak and Hirsfelder,[41] Kolos,[37] and Bishop and Cheng.[43] To demonstrate some theoretical results let us consider the nonrelativistic Hamiltonian for an N-electron diatomic molecule in a laboratory-fixed axis

$$H_{tot} = -\frac{1}{2M_a}\nabla_a^2 - \frac{1}{2M_b}\nabla_b^2 - \frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 + V \tag{3.19}$$

where a and b represent two nuclei with masses M_a and M_b while i labels the electrons. The vector position of CM is expressed as follows:

$$\mathbf{R}_{CM} = M^{-1}(M_a\mathbf{r}_a + M_b\mathbf{r}_b + \sum_{i=1}^{N}\mathbf{r}_i) \tag{3.20}$$

where

$$M = M_a + M_b + N \tag{3.21}$$

The separation of the CM motion from the internal motion can be accomplished using one of the following sets of coordinates:

(a) separated-atom coordinates[41,37]

$$\mathbf{R} - \mathbf{r}_b - \mathbf{r}_a \tag{3.22}$$

$$\mathbf{r}_{ia} = \mathbf{r}_i - \mathbf{r}_a \qquad 1 \le i \le N_a \tag{3.23}$$

$$\mathbf{r}_{jb} = \mathbf{r}_j - \mathbf{r}_b \qquad N_a + 1 \le j \le N \tag{3.24}$$

(b) center-of-mass of nuclei relative coordinates[41,37]

$$\mathbf{r}_{i(ab)} = \mathbf{r}_i - (M_a\mathbf{r}_a + M_b\mathbf{r}_b)(M_a + M_b)^{-1} \tag{3.25}$$

(with $\mathbf{R}_{CM}$ defined as previously), and

(c) Geometrical center of nuclei coordinates[41,37]

$$\mathbf{R} = \mathbf{r}_b - \mathbf{r}_a \tag{3.26}$$

$$\mathbf{r}_{ig} = \mathbf{r}_i - {}^1/_2(\mathbf{r}_a + \mathbf{r}_b) \tag{3.27}$$

The separation of the angular motion of the nuclei can be done by transforming from the space-fixed axis system (x,y,z) to a set of rotating molecule-fixed axes. The transformation is defined by the two Euler rotations: (i) ϕ about the initial z axis and (ii) θ about the resultant y axis:

$$R(\phi,\theta,0) = \begin{matrix} \cos\theta\cos\phi & \cos\theta\sin\phi & -\cos\theta \\ -\sin\phi & \cos\phi & 0 \\ \sin\theta\cos\phi & \sin\theta\sin\phi & \cos\theta \end{matrix} \tag{3.28}$$

The coordinates R, θ, and ϕ are sufficient to describe the motion of the nuclei. Separation of the CM motion and the rotation leads to a set of coupled equations. The coupling results from the fact that the geometrical center of the molecule and the CM for the nuclei do not coincide exactly with the center for the rotation. Nonadiabatic effects are incorporated by appropriate coupling matrix elements. More detail can be found in papers cited earlier, *i.e.*, refs 36, 37, and 43 as well as refs 10 and 39–42.

We would like to stress that the above approach should only work for systems that do not significantly violate the BO approximation and where the rigid rotor model remains a reasonably good approximation.

C. Many-Particle Systems

This subsection is devoted to nonadiabatic studies of polyatomic systems. We would like to distinguish two aspects of this problem; the first one is related to the development of theory and the second pertains to practical realizations. Some general aspects have been presented in the first part of this section. One of the most constructive nonadiabatic view of molecules and critical discussion of the BO approximation has been presented by Essen.[14] The starting point for his consideration was the virial theorem which, following Wooley's earlier study,[5] plays an essential role in understanding the nature of molecular systems. Essen demonstrated a quite original view on molecules. This view was later extensively analyzed by Monkhorst.[15] Let us use an excerpt from Monkhorst's paper:

> Invoking only the virial theorem for Coulombic forces and treating all particles on an equal footing, a molecule according to Essen can be viewed as an aggregate of nearly neutral subsystems ("atoms") that interact weakly ("chemical bonds") in some spatial arrangement ("molecular structure"). No adiabatic hypothesis is made, and the analysis should hold for all bound states.

According to Essen's work, the motion of a particle in the molecule consists of three independent motions: (1) the translational motion of the molecule as a whole, (2) the collective motion of the neutral subsystem, and (3) the individual, internal motion in each "atom". Individual motions of electrons and nuclei are not considered. The above classification allowed him to express coordinates of any particle in the molecule as

$$\mathbf{r}_i = \mathbf{R} + \mathbf{r}^C_{\gamma(i)} + \mathbf{r}^I_i \tag{3.29}$$

where $\mathbf{R}$ defines the position of the molecular CM with respect to a stationary coordinate system, and $\gamma(i) = \alpha$ if particle i belongs to the αth composite subsystem. The vector $\mathbf{r}^C_\gamma$ is the CM vector of the subsystem γ relative to the molecular CM, while $\mathbf{r}^I_i$ is the internal position of the particle i relative to CM of the subsystem to which it belongs. Essen's work provides an essential conceptual study of the BO approximation.

To demonstrate some practical aspects of Essen's theory, discussed also by Monkhorst,[15] let us consider an N-particle system. In principle, one can reduce the N-body problem to an $(N-1)$-body problem by the CM elimination which is easily achieved by coordinate transformation as described before. In all approaches the transformed include coordinates of the CM vector, $\mathbf{R}_{CM}$. The remaining coordinates of the set are internal coordinates that can be defined, for example, with respect to CM as

$$\rho_i = \mathbf{r}_i - \mathbf{R}_{CM} \qquad (i = 1,2,...,N) \tag{3.30}$$

However, since

$$\rho_N = -\frac{1}{m_N}\sum_{i=1}^{N-1} m_i\rho_i \tag{3.31}$$

the coordinates $(\rho_1,...,\rho N,\mathbf{R}_{CM})$ are linearly dependent.

One can avoid the linear dependence between internal coordinates by defining them with respect to any one of the N particles as suggested by Girardeau[47]

$$\rho_i = \mathbf{r}_i - \mathbf{r}_N \qquad (i = 1,...,N-1) \tag{3.32}$$

This is an extension of coordinate transformation used for three-particle systems. The set also includes the position vector of CM, $\mathbf{R}_{CM}$. There are still other coordinate sets that can be used, for example polyspherical coordinates.[45].

One can recognize that the discussed transformations are particular cases of eq 3.4. it is rather easy to demonstrate that the Hamiltonian expressed in terms of the new coordinates is still invariant under translational and orthogonal transformations of those coordinates. However, it is not easy to see that permutational invariance is maintained. This is due to the fact, that the space-fixed Hamiltonian contains inverse effective mass, and the particular form of f_{ij} depends on the choice of $\mathbf{U}$. It should be mentioned also, that the Hamiltonian after transformation has $3(N-1)$ space-fixed variables and, due to the nature of μ^{-1} and

the form of f_{ij}, it is usually difficult to interpret it in simple particle terms.

Another interesting nonadiabatic approach to multiparticle systems known as the generator coordinate method (GCM) has been proposed by Lathouwers and van Leuven.[48,49] The main idea of the GCM method is replacement of the nucleus coordinates in the BO electronic wave function by so called generator coordinates. The GCM represents conceptually an important approach in breaking with the BO approximation, unfortunately with little computational realization.

Finally, let us point out some common features of the nonadiabatic theory with the theory of highly excited rovibrational states, the theory of floppy molecules, the theory of molecular collisions, and the dynamics of van der Waals complexes.[45] The starting point of considerations on such types of systems is the nuclear Hamiltonian

$$\hat{H}_N = \sum_{i=1}^{N} \hat{T}_i + V(\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_N) \qquad (3.33)$$

where the first term, expressed in terms of $3N$ nuclear coordinates, represents the kinetic energy, while the second term represents the potential hypersurface. Analogous to the nonadiabatic approaches discussed before, the separation of the translational degrees of freedom is accomplished by a coordinate transformation. The new internal coordinates are translation free.[45,46] The second step involves transformation from the space-fixed coordinates to body-fixed coordinates. After such a transformation the internal wave function, which is dependent on the $3N - 6$ translationally and rotationally invariant coordinates, is usually determined in a variational calculation. This wave function represents the internal vibrational motion of the molecule. The selection of an appropriate coordinate system represents one of the most difficult theoretical problems in attempts to solve eq 3.24. (The relevant discussion on this subject can be found in ref 46.)

IV. Nonadiabatic Many-Body Wave Function

In the following section we will discuss an example of how, in practice, a nonadiabatic calculation on N-particle system can be accomplished. From the general considerations presented in the previous section one can expect that the many-body nonadiabatic wave function should fulfill the following conditions: (1) All particles involved in the system should be treated equivalently. (2) Correlation of the motions of all the particles in the system resulting from Coulombic interactions as well as from the required conservation of the total linear and angular momenta should be explicitly incorporated in the wave function. (3) Particles can be distinguished only via the permutational symmetry. (4) The total wave function should possess the internal and translational symmetry properties of the system. (5) For fixed positions of nuclei the wave functions should become equivalent to what one obtains within the Born–Oppenheimer approximation. (6) The wave function should be an eigenfunction of the appropriate total spin and angular momentum operators.

The most general expansion which can facilitate fulfillment of the above conditions has the form

$$\Psi_{tot} = \sum_{\mu=1}^{K} c_\mu P(1,2,...,N)[\omega_\mu(\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_N)\Theta^N_{S,M}], \qquad (4.1)$$

where ω_μ and $\Theta^N_{S,M}$ represent the spatial and spin components respectively. In the above expansion, we schematically indicate that each ω_μ should possess appropriate permutational properties, which is accomplished via an appropriate form of the permutation operator $P(1,2,...,N)$. The total wave function should be also an eigenfunction of the $\hat{S}^2$ and $\hat{S}_z$ spin operators which is accomplished by an appropriate form of the spin wave function $\Theta^N_{S,M}$.

Different functional bases have been proposed for nonadiabatic calculations on three-body systems, however extension to many particles has been difficult for the following reason: Due to the nature of the Coulombic two-body interactions the spatial correlation should be included explicitly in the wave function, *i.e.*, interparticle distances should be incorporated in the basis functions. Unfortunately, for most types of explicitly correlated wave functions the resulting many-electron integrals are usually difficult to evaluate. An exception is the basis set of explicitly correlated Gaussian geminals which contain products of two Gaussian orbitals and a correlation factor of the form $\exp(-\beta r_{ij}^2)$. These functions were introduced by Boys[50] and Singer.[51] The correlation part effectively creates a Coulomb hole, *i.e.*, reduces or enhances the amplitude of the wave function when two particles approach one another. The application of the explicitly correlated Gaussian geminals is not as effective as other types of correlated functions due to a rather poor representation of the cusp. However, such functions form a mathematically complete set,[52] and all required integrals have closed forms as was demonstrated by Lester and Krauss.[53] During the last three decades explicitly correlated Gaussian geminals have been successfully applied to different problems as, for example, in the calculations of the correlation energy for some closed-shell atoms and molecules, intermolecular interaction potentials, polarizabilities, Compton profiles, and electron-scattering cross sections.[54–61] Explicitly correlated Gaussian geminals were also applied to minimize the second-order energy functional in the perturbation calculation of the electronic correlation energy. First, Pan and King[62] demonstrated that rather short expansions with appropriate minimizations of nonlinear parameters lead to very accurate results for atoms. The same idea was later extended to molecular systems by Adamowicz and Sadlej.[63–69] We should also mention a series of papers by Monkhorst and co-workers[70–74] where explicitly correlated Gaussian geminals were used in conjunction with the second-order perturbation theory and the coupled cluster method.

In the remainder of this section we would like to describe an application of the explicitly correlated Gaussian-type functions to nonadiabatic calculations on a multiparticle system. The explicitly correlated Gaussian functions form a convenient basis set for multiparticle nonadiabatic calculations because, due to the separability of the squared coordinates, the integrals over Gaussian functions are relatively easy to evaluate. As a consequence, one can afford to use a larger number of these functions in the basis set than in cases of explicitly correlated functions of other types.

In a nonadiabatic calculation the spatial part of the ground state N-particle wave function (eq 4.1) can be expanded in terms of the following explicitly correlated Gaussian functions (which will be called Gaussian cluster functions):

$$\omega_\mu = \exp(-\sum_{i=\mu}^{N}\alpha_i^\mu|\mathbf{r}_i - \mathbf{R}_i^\mu|^2 - \sum_{i=1}^{N}\sum_{j>i}^{N}\beta_{ij}^\mu|\mathbf{r}_i - \mathbf{r}_j|^2) \quad (4.2)$$

Each ω_μ depends on the following parameters: α_i^μ, $\mathbf{R}_i^\mu$, and β_{ij}^μ (the orbital exponents, the orbital positions, and the correlation exponents, respectively). The centers need not coincide with the positions of the nuclei. After some algebraic manipulations the correlation part may be rewritten in the following quadratic form:

$$\omega_\mu = \exp(-\sum_{i=1}^{N}\alpha_i^\mu|\mathbf{r}_i - \mathbf{R}_i^\mu|^2 - \mathbf{r}\mathbf{B}^\mu\mathbf{r}^T) \quad (4.3)$$

where the vector $\mathbf{r}$ is equal to

$$\mathbf{r} = (\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_N) \quad (4.4)$$

and the matrix $\mathbf{B}^\mu$ is constructed with the use the correlation exponents ($\beta_{ii}^\mu = 0$)

$$\mathbf{B}^\mu = \begin{pmatrix} \sum_{j=1}^{N}\beta_{1j}^\mu & -\beta_{12}^\mu & \cdots & -\beta_{1N}^\mu \\ -\beta_{12}^\mu & \sum_{j=1}^{N}\beta_{2j}^\mu & \cdots & -\beta_{2N}^\mu \\ \vdots & \vdots & \ddots & \vdots \\ -\beta_{1N}^\mu & -\beta_{2N}^\mu & \cdots & \sum_{j=1}^{N}\beta_{Nj}^\mu \end{pmatrix} \quad (4.5)$$

The above form of the Gaussian cluster function is more convenient than the form given by eq 4.2 for evaluation of the molecular integrals which will be discussed in the next subsection.

The angular dependence of Gaussian functions can be achieved explicitly through the use of spherical harmonics, or equivalently through the use of integer powers of the appropriate Cartesian coordinates. In order to generate a Cartesian–Gaussian, an s-type cluster is multiplied by an appropriate power of the coordinates of the particle positions with respect to the orbital centers

$$\phi_\mu(\{l_p^\mu,m_p^\mu,n_p^\mu\},\{\mathbf{r}_p\},\{\mathbf{R}_p^\mu\},\{a_p^\mu\},\{b_{pq}^\mu\}) = \prod_{p=1}^{N}[(x_p - R_{p,x}^\mu)_p^{l_\mu}(y_p - R_{p,y}^\mu)_p^{m_\mu}(z_p - R_{p,z}^\mu)_p^{n_\mu}]\omega_\mu \quad (4.6)$$

where $\{l_p^\mu,m_p^\mu,n_p^\mu\}$ will be called the "angular momentum" of the Gaussian cluster function (constructed similarly as for the orbital Gaussians).

A. Many-Particle Integrals

In this section we would like to discuss evaluation of many-particle integrals over explicitly correlated Gaussian functions which are required for our method of nonadiabatic calculations. The simplicity of the appropriate algorithms for molecular integrals leading to efficient computation implementations represents one of the most important elements in the development of an effective nonadiabatic methodology. The integral procedures are quite general and can be extended to an arbitrary number of particles. To avoid unnecessary details we will first demonstrate the general strategy for calculating integrals with spherical Gaussians. Next we will discuss how the procedure can be extended to Gaussians with higher angular momenta. The details of evaluation of molecular integrals over general Gaussian cluster functions can be found in our previous papers.[75,76]

Let us consider a general matrix element containing two Gaussian cluster functions $\langle\omega_\mu|\hat{O}|\omega_\nu\rangle$, where $\hat{O}$ represents a one-body operator $\hat{O}(i)$, or a two-body operator $\hat{O}(i,j)$. (Omitted from the present discussion is the kinetic energy integral and operators containing differentiation which will be described later.)

$$\langle\omega_\mu(\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_N)|\hat{O}(i,j)|\omega_\nu(\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_N)\rangle = \int\int...\int \exp(-\sum_{n=1}^{N}\alpha_n^\mu|\mathbf{r}_n - \mathbf{R}_n^\mu|^2 - \mathbf{r}\mathbf{B}^\mu r^T) \times \hat{O}(i,j) \exp(-\sum_{n=1}^{N}\alpha_n^\nu|\mathbf{r}_n - \mathbf{R}_n^\nu|^2 - \mathbf{r}\mathbf{B}^\nu\mathbf{r}^T)d\mathbf{r}_1\,d\mathbf{r}_2...d\mathbf{r}_N \quad (4.7)$$

In general, the above multiparticle integral is a many-center integral. In the first step, the well-known property of the Gaussian orbitals is used to combine two Gaussian functions located at two different centers to a Gaussian function at a third center

$$\omega_\mu\omega_\nu = K_{\mu\nu}\omega_{\mu\nu} \quad (4.8)$$

where

$$K_{\mu\nu} = \exp\left(-\sum_{n=1}^{N}\frac{\alpha_n^\mu\alpha_n^\nu}{\alpha_n^\mu + \alpha_n^\nu}|\mathbf{R}_n^\mu - \mathbf{R}_n^\nu|^2\right) \quad (4.9)$$

The integral $\langle\omega_\mu|\hat{O}|\omega_\nu\rangle$ takes the form

$$\langle\omega_\mu|\hat{O}|\omega_\nu\rangle = K_{\mu\nu}\int\int...\int \hat{O}\exp(-\sum_{n=1}^{N}\alpha_n^{\mu\nu}|\mathbf{r}_n - \mathbf{R}_n^{\mu\nu}|^2 - \mathbf{r}\mathbf{B}^{\mu\nu}\mathbf{r}^T)\,d\mathbf{r}_1d\mathbf{r}_2...d\mathbf{r}_N. \quad (4.10)$$

For simplicity and compactness of the notation we used the abbreviation $a_n^{\mu\nu} = \alpha_n^\mu + \alpha_n^\nu$, and $\mathbf{B}^{\mu\nu} = \mathbf{B}^\mu + \mathbf{B}^\nu$. Let us now rewrite the last integral in a slightly different way and explicitly separate the $G(\mathbf{r}_i,\mathbf{r}_j)$ function

$$\langle\omega_\mu|\hat{O}|\omega_\nu\rangle = K_{\mu\nu}\int\int\hat{O}(i,j)G(\mathbf{r}_i,\mathbf{r}_j)\exp(-a_i^{\mu\nu}|\mathbf{r}_i - \mathbf{R}_i^{\mu\nu}|^2)\exp(-\alpha_j^{\mu\nu}|\mathbf{r}_j - \mathbf{R}_j^{\mu\nu}|^2)\,d\mathbf{r}_i\,d\mathbf{r}_j \quad (4.11)$$

The $G(\mathbf{r}_i,\mathbf{r}_j)$ function contains all the information about the correlation part and is defined as follows:

$$G(\mathbf{r}_i,\mathbf{r}_j) = \int\int...\int \exp(-\sum_{n=1\,n\neq i\neq j}^{N}\alpha_n^{\mu\nu}|\mathbf{r}_n - \mathbf{R}_n^{\mu\nu}|^2 - \mathbf{r}\mathbf{B}^{\mu\nu}\mathbf{r}^T)\prod_{k=1\,n\neq i\neq j}^{N}d\mathbf{r}_k \quad (4.12)$$

It should be pointed out that, if the elements of the correlation matrix $\mathbf{B}^{\mu\nu}$ are equal to zero, the G function becomes simply a product of overlap integrals over Gaussian orbitals. Evaluation of $G(\mathbf{r}_i,\mathbf{r}_j)$ concludes the reduction of the $3N$-dimension integration to a 6-di-

mension integration in the case when $\hat{O}$ is a two-body operator. In the case of a one-body operator we additionally integrate the G function over the $\mathbf{r}_j$ coordinate, $G(\mathbf{r}_i) = \int G(\mathbf{r}_i,\mathbf{r}_j)\, d\mathbf{r}_j$. The function G can be evaluated for an arbitrary number of particles. It is important to notice that by determining the G function, the multiparticle integral is reduced to an integral that contains Gaussian geminals instead of the N-particle Gaussian cluster functions. The integration over all coordinates except i and j we called "reduction". The integrals with Gaussian geminals can be evaluated using the Fourier transform technique and the convolution theorem as was demonstrated by Lester and Krauss[53] as well as by us for general types of integrals.[75]

So far considerations have been restricted to spherical Gaussian functions. To calculate nonadiabatic states with higher angular momenta the Cartesian–Gaussian functions need to be used in the wave function expansion. To obtain Gaussian functions corresponding to higher angular momenta we applied the procedure which is based on the observation that the Cartesian factors in the function can be generated by consecutive differentiations of the s-type Gaussian function with respect to the coordinates of the orbital centers. This leads to a direct generalization of the integral algorithms derived for the s-type cluster functions to algorithms for the Cartesian cluster functions. This involves expressing the functions with higher angular momenta in terms of raising operators as follows:

$$\phi_\mu(\{l_i^\mu,m_i^\mu,n_i^\mu\},\{\mathbf{r}_p\},\{\mathbf{R}_p^\mu\},\{a_p^\mu\},\{b_{pq}^\mu\}) = \prod_{p=1}^{N}[\hat{M}_x^{l_p^\mu}\hat{M}_y^{m_p^\mu}\hat{M}_z^{n_p^\mu}]\omega_\mu \quad (4.13)$$

where the raising operator, $\hat{M}^n$, is expressed as a series of partial derivatives with respect to the coordinates of the orbital center

$$\hat{M}_x^n = \sum_{m=0}^{[n/2]} C_m^n \frac{\partial^{n-2m}}{\partial R_x^{n-2m}} \quad (4.14)$$

and

$$C_m^n = \frac{n!}{2^n\alpha^{n-m}m!\,(n-2m)!} \quad (4.15)$$

This form of the raising operators was used by Schlegel[77,78] for computation of the second derivatives of the two-electron integrals over s and p Cartesian orbital Gaussians. If the operator $\hat{O}$ commutes with the Gaussian function the integral can be rewritten as

$$O_{\mu\nu} = K_{\mu\nu}\int\int\ldots\int \hat{O}\phi_{\mu\nu}\prod_{p=1}^{N} d\mathbf{r}_p \quad (4.16)$$

and according to the previous considerations becomes

$$O_{\mu\nu} = K_{\mu\nu}\prod_{p=1}^{N}[\hat{M}_x^{l_p^\mu}\hat{M}_y^{m_p^\mu}\hat{M}_z^{n_p^\mu}]\int\int\ldots\int \hat{O}\omega_{\mu\nu}\prod_{p=1}^{N} d\mathbf{r}_p \quad (4.17)$$

The last expression contains only integrals with the spherical functions.

Using the above scheme we can evaluate the overlap integral, the nuclear attraction integral, and the electron repulsion integral. The procedure cannot be, however, directly applied to the kinetic energy integral. It is necessary to first express this integral as a linear combination of some overlap integrals and subsequently use the raising operator approach. The details and practical realization of the above scheme have been described in ref 76.

V. Effective Nonadiabatic Method

The nonadiabatic wave function expanded in terms of Gaussian cluster functions has been used by Poshusta and co-workers in nonadiabatic calculations of three particle systems.[22] The treatment was recently extended to four particles.[79] Poshusta's approach has been based on the separation of the CM motion from the internal motion through transformation to the CM coordinate system. In our recent work we have taken a different approach which has been based on an effective rather than explicit separation of the CM motion. To demonstrate the essential points of this approach, let us consider an N-particle system with Coulomb interactions. The particle masses and charges are $(m_1,m_2,\ldots,m_N)$ and $(Q_1,Q_2,\ldots,Q_N)$, respectively. Neglecting the relativistic effects and in the absence of external fields, the system is described by the Hamiltonian

$$H_{tot} = \sum_{i=1}^{N}\frac{p_i^2}{2m_i} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{Q_iQ_j}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (5.1)$$

where P_i and $\mathbf{r}_i$ are the momentum and positions vectors. Let us also consider a general coordinate transformation,

$$(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N) \rightarrow (\mathbf{R}_{CM},\rho_1,\ldots,\rho_{N-1}) \quad (5.2)$$

which allows separation of the CM motion from the internal motion, *i.e.*, explicitly separate the total Hamiltonian into the internal Hamiltonian, H_{int}, and the Hamiltonian for the CM motion, $T_{CM} = p_{CM}^2/2m$;

$$H_{tot} = H_{int} + T_{CM} \quad (5.3)$$

Due to this separation, the total wave function can always be represented as a product of the internal part and the wave function for the CM motion

$$\Psi_{tot} = \Phi_{CM}\Phi_{int} \quad (5.4)$$

Instead of an explicit separation let us now consider the following variational functional:

$$J[\Psi_{tot};k] = \frac{\langle\Psi_{tot}|H_{tot}|\Psi_{tot}\rangle + k\langle\Psi_{tot}|T_{CM}|\Psi_{tot}\rangle}{\langle\Psi_{tot}|\Psi_{tot}\rangle} \quad (5.5)$$

where k is an arbitrary constant which scales the positive term that represents the kinetic energy of the motion of the center of mass. Both operators, *i.e.*, the total Hamiltonian, H_{tot}, and the kinetic energy of the CM motion, T_{CM}, have simple forms in the Cartesian coordinate system. By minimizing the functional $J[\Psi_{tot},k]$ with positive values for k, the kinetic energy of the CM motion can be forced to become much smaller than the internal energy of the system. In order to perform a meaningful nonadiabatic variational calculation the kinetic energy contributions need to be reduced and made as insignificant as possible in comparison to the internal energy. For larger k values, more emphasis in the optimization process is placed on

reducing the magnitude of

$$\frac{\langle\Psi_{tot}|T_{CM}|\Psi_{tot}\rangle}{\langle\Psi_{tot}|\Psi_{tot}\rangle}$$

In our calculations the value for k has been selected based on the accuracy we wanted to achieve in determining the internal energy of the system. The approach based on minimizing the expectation value of T_{CM} will be called method I in our further discussion.

There is an alternative scheme to nonadiabatic calculation which we will call method II. Let us examine the case when the k parameter is set to -1 in eq 5.5. The functional becomes

$$J[\Psi_{tot};-1] = \frac{\langle\Psi_{tot}|H_{tot} - T_{CM}|\Psi_{tot}\rangle}{\langle\Psi_{tot}|\Psi_{tot}\rangle} = \frac{\langle\Psi_{tot}|H_{int}|\Psi_{tot}\rangle}{\langle\Psi_{tot}|\Psi_{tot}\rangle} \tag{5.6}$$

The full optimization effort can now be directed solely to improving the internal energy of the system because the functional eq 5.6 now contains only the internal Hamiltonian. One can expect that after optimization the variational wave function will be a sum of products of the integral ground state and wave functions representing different states of the CM motion:

$$\Psi_{tot} - \Psi_{int}\sum_i a_i\phi^i_{CM} \tag{5.7}$$

However, since the internal Hamiltonian only acts on the internal wave function, the variational functional, $J[\Psi_{tot};-1]$, becomes

$$\min\{J[\Psi_{tot};-1]\} = \min\left\{\frac{\langle\Psi_{int}|H_{tot} - T_{CM}|\Phi_{int}\rangle}{\langle\Phi_{int}|\Phi_{int}\rangle}\right\} \tag{5.8}$$

with according to the variational principle is

$$\min\{J[\Psi_{tot};-1]\} \geq E_{int} \tag{5.9}$$

Therefore in method II, by minimization of the functional eq 5.6, one obtains directly an upper bound to the internal energy of the system. In this case the kinetic energy of the CM motion is not minimized.

In the above considerations we demonstrated that the internal energy can be separated from the total energy of the system without an explicit transformation to the CM coordinate system. This is an important point since an inappropriate elimination of the CM can lead to so-called "spourus" states,[44] which in turn lead to contradictory results in nonadiabatic calculations.

The last element which we would like to demonstrate is that the variational wave function in the form eq 4.2 can be formally separated into a product of an internal wave function and a wave function of the CM motion. This is mandatory for any variational nonadiabatic wave function in order to provide required separability of the internal and external degrees of freedom. To demonstrate this let us consider an N-particle system with masses $m_1,m_2,...,m_N$. An example of a wave function for this system which separates to a product of the internal and external components is

$$\Psi_{tot} = \exp(-\eta\mathbf{R}^2_{CM})\sum_k C_k \exp(-\sum_{i=1}^{N}\sum_{j>i}^{N}\gamma^k_{ij}r^2_{ij}) \tag{5.10}$$

It can be shown that with the use of the matrices

$$\tilde{\mathbf{M}} = \frac{\eta}{M^2}\begin{pmatrix} \sum_{j=1}^{N}\gamma^k_{1j} & -\gamma^k_{12} & \cdots & -\gamma^k_{1N} \\ -\gamma^k_{12} & \sum_{j=1}^{N}\gamma^k_{2j} & \cdots & -\gamma^k_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ -\gamma^k_{1N} & -\gamma^k_{2N} & \cdots & \sum_{j=1}^{N}\gamma^k_{Nj} \end{pmatrix} \tag{5.11}$$

and

$$\mathbf{\Gamma}_k = \begin{pmatrix} m_1^2 & m_1m_2 & \cdots & m_1m_N \\ m_1m_2 & m_2^2 & \cdots & m_2m_N^k \\ \vdots & \vdots & \ddots & \vdots \\ m_1m_N & -m_2m_N & \cdots & m_N^2 \end{pmatrix} \tag{5.12}$$

the total wave function, Ψ_{tot}, can be represented as

$$\Psi_{tot} = \sum_k C_k \exp(-(\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_N)(\tilde{\mathbf{M}} + \mathbf{\Gamma}_k)(\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_N)^T) \tag{5.13}$$

which has the same form as the function eq 4.2 with $\mathbf{R}^k_i = 0$ and $A^k_{ij} = \delta_{ij}\alpha^k_i$, *i.e.*,

$$\Psi_{tot} = \sum_k C_k \exp(-(\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_N)(\mathbf{A}^k + \mathbf{B}^k)(\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_N)^T) \tag{5.14}$$

The main idea of the above methodology rests in treating nonadiabatically the N-particle problem in the Cartesian space without reducing it to an $(N-1)$-particle problem by explicit separation of the CM motion. One can ask what advantage does this approach have in comparison to the conventional one? One clear advantage is that we avoid selecting an internal coordinate system—a procedure that is not unique and may lead to certain ambiguities. The work in the Cartesian space makes the physical picture more intuitive and the required multiparticle integrals are much easier to evaluate. Those two features certainly are not present if more complicated coordinate systems such as in polyspherical coordinates[45] are used. Also, we noted earlier that the other factor which should be taken into consideration is the proper "ansatz" for the trial variational wave function incorporating the required permutational symmetry. In our approach the appropriate permutational symmetry is easy to implement through direct exchange of the particles in the orbital factors and the correlation components. This task, however, can be complicated when one works with a transformed coordinate system. The last problem which should be taken into consideration relates to the rotational properties of the wave function. Definitions of the appropriate rotational operators in terms of the Cartesian coordinates are straightforward. However, in a transformed coordinate system the operators representing the rotation of the system about its CM can be complicated and may lead to significant difficulties in calculating the required matrix elements.

VI. Numerical Examples

A. Positronium and Quadronium Systems

In this section we would like to discuss numerical results for two model systems: positronium, *Ps*, and

Table I. Ground-State Energies Computed with Different k Values for the e^+e^- [a]

k	$\min\{J[\Psi;k]\}$	E_{int} [b]	T_{CM}
		Method I	
1	−0.249 947 0	−0.249 969 5	$2.252\,4 \times 10^{-5}$
100	−0.248 962 3	−0.249 602 6	$6.403\,6 \times 10^{-6}$
		Method II	
−1	−0.249 996 2	−0.249 996 2	$5.013\,5 \times 10^{-5}$

[a] Energies in atomic units. [b] For method II, $E_{int} = \min\{J[\Psi,-1]\}$. For method I, $E_{int} = \min\{J[\Psi,0]\}$.

quadronium, Ps_2. Although, there is certainly not much chemical interest in these systems, they constitute ideal cases to verify the performance on nonadiabatic methodologies. The nonrelativistic quantum mechanics for positronium system is exactly the same as for the hydrogen atom, except the value of reduced mass. The positronium system (e^+e^-) is strongly nonadiabatic and represents an excellent simple test case since its nonrelativistic ground-state energy can be determined exactly ($E_{gs} = -0.25$ au). Contrary to the hydrogen atom, the Born–Oppenheimer approximations cannot be used.

In the method we have developed the nonadiabatic wave function for the positronium system depends on all six cartesian coordinates of the electron and the positron as well as on their spin coordinates. For numerical calculations the following fourteen-term variational wave function was used:

$$\Psi_{tot} = \sum_{i=1}^{14} C_i \exp(-\alpha_1^i r_1^2 - \alpha_2^i r_2^2 - \beta_{12}^i r_{12}^2)\Theta(e^-)\Theta(e^+) \quad (6.1)$$

The minimization of the variational functional eq 5.5 was performed with different values of k. The results of the calculations are summarized in Table I.

Upon examining numerical values it seems that both methods I and II provide similar results in close agreement with the exact value mainly dependent on the length of the expansion of the wave function. However, for the same expansion length, Method II seems to perform better and converge faster.

As the second example, let us consider the quadronium system composed of two electrons and two positrons. The complete nonrelativistic Hamiltonian for the Ps_2 system reads

$$H_{tot} = -\tfrac{1}{2}(\nabla_1^2 + \nabla_2^2 + \nabla_A^2 + \nabla_B^2) + \frac{1}{r_{12}} + \frac{1}{r_{AB}} - \frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} \quad (6.2)$$

where 1 and 2 denote the electrons, and A and B the positrons, respectively. Similar to the positronium case no approximation can be made with regard to the separability of the internal motions of the particles. The standard approach to find the nonadiabatic solution is based on separation of the center-of-mass motion from the internal motion as described in the section III.A. Introducing internal coordinates as the position vectors of three particles with respect to the fourth particle chosen as the reference, the four-particle problem can be reduced to the problem of three fictitious pseudoparticles. As discussed before, after transformation to the new coordinates, the internal Hamiltonian contains additional terms known as mass polarization terms, which arise due to the nonorthogonality of the new coordinates. Using the above transformation Kinghorn and Poshusta[79] carried out nonadiabatic variational calculations with Singer polymass basis set functions. The Singer polymass basis set has the following form:

$$f_k(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) = \exp[-(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)\mathbf{Q}^k(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)^T] \quad (6.3)$$

where matrix $\mathbf{Q}^k$ contains nonlinear parameters, subject of optimization. The total nonadiabatic wave function in Kinghorn's and Poshusta's calculations had the following form:

$$\Psi_{non}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) = \sum_{k=1}^{M} C_k[P(1,2,3)\omega_k(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)\Theta(1,2,3)] \quad (6.4)$$

where $P(1,2,3)$ denotes the permutational operator which enforces the antisymmetry of the wave function with respect to interchanging of the identical particles as well as the charge inversal symmetry between the positrons and the electrons.

Since in our approach no explicit separation of the center of mass is required, the quadronium system is represented by the wave function which explicitly depends on coordinates of all particles:

$$\Psi_{tot}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_A,\mathbf{r}_B) = \sum_{k=1}^{M} C_k[P(A,B)P(1,2)\omega_k(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_A,\mathbf{r}_B)]\Theta(A,B)\Theta(1,2) \quad (6.5)$$

with spatial function ω_k given as a one-center explicitly correlated Gaussian function

$$\omega_k(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_A,\mathbf{r}_B) = \exp(-\alpha_1^k r_1^2 - \alpha_2^k r_2^2 - \alpha_A^k r_A^2 - \alpha_B^k r_B^2 - \beta_{12}^k r_{12}^2 - \beta_{1A}^k r_{1A}^2 - \beta_{1B}^k r_{1B}^2 - \beta_{2A}^k r_{2A}^2 - \beta_{2B}^k r_{2B}^2 - \beta_{AB}^k r_{AB}^2) = \exp[-(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_A,\mathbf{r}_B)(\mathbf{A}^k + \mathbf{B}^k)(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_A,\mathbf{r}_B)^T] \quad (6.6)$$

where $\mathbf{A}^k$ and $\mathbf{B}^k$ are defined as follows:

$$\mathbf{A}^k = \begin{pmatrix} \alpha_1^k & 0 & 0 & 0 \\ 0 & \alpha_2^k & 0 & 0 \\ 0 & 0 & \alpha_A^k & 0 \\ 0 & 0 & 0 & \alpha_B^k \end{pmatrix} \quad (6.7)$$

$$\mathbf{B}^k = \begin{pmatrix} \beta_{12}^k+\beta_{1A}^k+\beta_{1B}^k & -\beta_{12}^k & -\beta_{1A}^k & -\beta_{1B}^k \\ -\beta_{12}^k & \beta_{12}^k+\beta_{2A}^k+\beta_{2B}^k & -\beta_{2A}^k & -\beta_{2B}^k \\ -\beta_{1A}^k & -\beta_{2A}^k & \beta_{1A}^k+\beta_{2A}^k+\beta_{AB}^k & -\beta_{AB} \\ -\beta_{1B}^k & -\beta_{2B}^k & -\beta_{AB}^k & \beta_{1B}^k+\beta_{2B}^k+\beta_{AB}^k \end{pmatrix} \quad (6.8)$$

The spin functions representing the electrno and positron singlets are given as

$$\Theta(A,B)\Theta(1,2) = \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]\frac{1}{\sqrt{2}}[\alpha(A)\beta(B) - \beta(A)\alpha(B)] \quad (6.9)$$

It is assumed that there is no spin coupling between the electrons and positrons. The spatial part of the wave function is symmetric with respect to exchanging electrons as well as positrons, which is achieved by the permutational operators $P(1,2) = (1,2) + (2,1)$ and $P(A,B) = (A,B) + (B,A)$. In the nonadiabatic wave function, motions of all particles are correlated through

Table II. Total and Binding Energies Calculated for the Quadronium System with a Different Number of Basis Functions Used in the Expansion of the Wave Function[a]

no. of functions	total energy	binding energy[b]
16	−0.510 762	0.293
32	−0.515 385	0.419
64	−0.515 852	0.431
128	−0.515 949	0.434
210	−0.515 974	0.435
300	−0.515 980	0.435

[a] The total energy is expressed in atomic units and binding energy in eV. (1 au = 27.211 396 1 eV.) [b] Exact energy of the e^+e^- system is equal to −0.25 au.

the squares of the interparticular distances present in the exponent. The center-of-mass motion is removed from the total Hamiltonian but not from the wave function. This leads to the following form of the variational functional:

$$J[\Psi_{tot}] = \frac{\langle \Psi_{tot}|H_{tot} - T_{CM}|\Psi_{tot}\rangle}{\langle \Psi_{tot}|\Psi_{tot}\rangle} = \frac{\langle \Psi_{tot}|H_{int}|\Psi_{tot}\rangle}{\langle \Psi_{tot}|\Psi_{tot}\rangle} \tag{6.10}$$

where

$$T_{CM} = \frac{1}{8}(\mathbf{p}_1 + \mathbf{p}_2 + \mathbf{p}_A + \mathbf{p}_B)^2 = \frac{1}{8}\sum_{i=1,2,A,B}^{4}\sum_{j=1,2,A,B}^{4}\nabla_i\nabla_j \tag{6.11}$$

Optimization of the functional has been performed with the variational wave function expanded in terms of 16, 32, 64, 128, 210, and 300 explicitly correlated Gaussian functions. The numerical conjugate gradient optimization technique was employed. To indicate the extent of the optimization effort involved, it suffices to say that, for example, for the wave function expanded into a series of 300 Gaussian functions one needs to optimize as many as 3000 exponential parameters. The results of the calculations are presented in Table II.

For all the expansion lengths considered, the optimizations were quite well converged, although with a large number of nonlinear parameters, one can almost never be sure whether a local or global minimum was reached or whether some more optimization would lead to further improvement of the results. Upon examining the convergence of the results with elongation of the expansion, one sees that the values of the bonding energy are quite well converged. Our best result for the total energy (−0.515 980 au)[87] is very close to the best result of Kinghorn and Poshusta (−0.515 977 au). It should be mentioned that both results are rigorously variational. Both energies lead to virtually identical bonding energies of the quadronium system with respect to the dissociation into two isolated *Ps* systems of 0.435 eV. Variational calculations for positronium molecule were also carried out by Ho.[89] This author used Hyleraas-type variational wave functions somewhat simplified to reduce some computational difficulties. His best variational energy of 0.411 eV is slightly higher then both Kinghorn and Poshusta's result and our result.

One important piece of information one can obtain from the nonadiabatic wave function pertains to the structure of the quadronium system. The answer requires calculation of averaged interparticular distances. For the wave function expressed in terms of explicitly correlated Gaussian functions the easiest to calculate are the averages of the squares of the distances. The results of such calculations for the Ps_2 molecule are presented in Table III.

Table III. Averaged Squares of the Interparticular Distances for the Quadronium System Calculated for Different Expansion Lengths of the Wave Function[a]

no. of functions	e^+e^+	e^+e^- $\langle r_{ij}^2\rangle$	e^-e^-
34	44.139	27.932	44.134
64	45.311	28.565	45.312
128	45.681	28.762	45.679
210	45.881	28.863	45.879
300	45.911	28.878	45.911

[a] Results in atomic units.

Table IV. Nonadiabatic Calculations on H, H_2^+, and H_2 Accomplished with Method II

no. of Gaussian cluster functions	total internal energy	exact or best literature value
	H	
14	−0.499 724	
		−0.499 729
	H_2^+	
14	−0.589 387	
16	−0.590 105	
20	−0.591 690	
32	−0.594 571	
64	−0.596 257	
104	−0.596 650	
205	−0.596 901	
		−0.597 139[a]
	H_2	
16	−1.142 988	
28	−1.148 156	
56	−1.155 322	
105	−1.160 202	
210	−1.162 369	
		−1.164 024[a]

[a] Reference 43.

Upon examining the results one notics that the $e^- - e^-$ distance is virtually the same as the $e^+ - e^+$ distance. This is a reflection of the charge reversal symmetry. The second observation is that the $e^+ - e^-$ distance is significantly shorter than the $e^+ - e^+$ and $e^- - e^-$ distances. This suggests that the Ps_2 molecule is a complex of two *Ps* systems.

B. H, H_2^+, and H_2 Systems

The other important question one may ask is how many Gaussian cluster functions are necessary to obtain satisfactory results for a few particle systems? To demonstrate this we performed a series of calculations for a sequence of simple systems, H, H_2^+ and H_2. The results are in Table IV.

Notice that with a short expansion we almost reproduced the exact nonrelativistic energy for the hydrogen atom. It takes only about 16 Gaussian cluster functions to lower the energy below −0.59 au for the H_2^+ molecule, and with 205 functions one gets already within 0.00024 au to the best nonrelativistic result of −0.597 139.[43] For H_2, which consists of four particles, we did calculations with 16, 28, 56, and 105 cluster functions. The results indicate that one should use at least 300 or more to obtain a result of comparable accuracy as the one achieved for H_2^+. The nonadiabatic

wave function representing the ground-state energy of the H_2 molecule had the following form:

$$\Psi_{tot}(A,B,1,2) = \sum_{k=1}^{M} C_k P(A,B)P(1,2)[\omega_k(\mathbf{r}_A,\mathbf{r}_B,\mathbf{r}_1,\mathbf{r}_2)]\Theta(A,B)\Theta(1,2) \quad (6.12)$$

where A,B are protons and 1,2 are electrons. Again we assumed that the coupling between nuclear and electron spins was negligible and, therefore, the spin function of the system is a product of the spin functions for the nuclei and the electrons. For the ground state, both spin functions $\Theta(A,B)$ and $\Theta(1,2)$ represent singlet states. The spatial basis functions are

$$\omega_k = \exp[-(\mathbf{r}_A,\mathbf{r}_B,\mathbf{r}_1,\mathbf{r}_2)(\mathbf{A}^k + \mathbf{B}^k)(\mathbf{r}_A,\mathbf{r}_B,\mathbf{r}_1,\mathbf{r}_2)^T] \quad (6.13)$$

where the matrix $(\mathbf{A}^k + \mathbf{B}^k)$ contains four orbital exponents in the diagonal positions and six correlation exponents. In such expansions all parameters, (*i.e.*, orbital and correlation exponents), are subject to optimization. This creates a problem one often encounters in variational nonadiabatic calculations for more extended systems with a larger number of basis functions: the necessity to optimize many nonlinear parameters. The next section deals with the approach we have taken in this area.

C. HD^+ Molecular Ion

The hydrogen molecular ion HD^+ has played an important role in development of molecular quantum mechanics. Many different methods have been tested on HD^+. Since the interelectronic interaction is not present, very accurate numerical results could be obtained. One of the most accurate nonadiabatic calculations was performed by Bishop and co-workers.[43] Bishop in his calculations used the following basis functions expressed in terms of elliptical coordinates with R being the nuclear separation:

$$\phi_{ijk}(\xi,\eta,R) = \exp(-\alpha\xi)\cosh(\beta\eta)\xi^i\eta^j R^{-3/2}\exp[{}^1/_2(-x^2)]H_k(x) \quad (6.14)$$

where $x = \gamma(R - \delta)$; $H_k(x)$ are Hermite polynomials; α, β, γ, and δ are adjustable parameters chosen to minimize the lowest energy level; and i, j, and k are integers. The energy obtained using this expansion was –0.597 897 967 au.)

In effective approach, without explicit separation od the center-of-mass motion, the nonadiabatic wave function for the HD^+ ion is expressed in terms of explicitly correlated Gaussian functions:

$$\Psi_{tot} = \sum_{k=1}^{M} c_k\omega_k(\mathbf{r}_D,\mathbf{r}_H,\mathbf{r}_e)\Theta(D)\Theta(H)\Theta(e) \quad (6.15)$$

where $\Theta(D)$, $\Theta(H)$, and $\Theta(e)$ represent the spin functions for deuteron, proton, and electron respectively, and the spatial basis functions are defined as

$$\omega_k = \exp[-\alpha_D^k r_D^2 - \alpha_H^k r_H^2 - \alpha_e^k r_e^2 - \beta_{HD}^k r_{HD}^2 - \beta_{He}^k - \beta_{De}^k r_{De}^2] \quad (6.16)$$

where $\mathbf{r}_D$, $\mathbf{r}_H$, and $\mathbf{r}_e$ are the position vectors of the deuteron, the proton, and the electron, respectively, and $\mathbf{r}_{HD}$, $\mathbf{r}_{He}$, $\mathbf{r}_{De}$ denote the respective interparticular distances.

Table V. Ground-State Internal Energies (in au) Computed with Basis Set of M Functions for the HD^+ Molecule

M	E_{min}[a]
10	–0.562 111
18	–0.586 854
36	–0.593 885
50	–0.595 369
60	–0.595 665
100	–0.596 435
200	–0.596 806

[a] The best literature value = –0.597 897 967.

Table VI. Expectation Values of the Square of the Interparticle Separations (in au) Computed with Basis Sets of Different Lengths (M) for the HD^+ Molecule

M	$\langle r^2_{HD}\rangle$	$\langle r^2_{He}\rangle$	$\langle r^2_{De}\rangle$
60	4.479 4	3.631 2	3.631 8
100	4.411 9	3.598 2	3.590 6
200	4.314 5	3.554 9	3.551 7

The values of the total ground-state energy of HD^+ calculated with Gaussian basis set of different lengths are presented in Table V.

One can see a consistent convergence trend with the increasing number of functions. Comparing our best result obtained with 200 Gaussian functions of –0.596 806 au with the result of Bishop and Cheung, –0.597 898 au, indicates that more Gaussian functions will be needed to reach this result with our method.

Following evaluation of the HD^+ ground-state wave function we calculated the expectation values of the squares of interparticular distances. The HD^+ system should possess slight asymmetry in the values for $\langle r^2_{He}\rangle$ and $\langle r^2_{De}\rangle$ leading to a permanent dipole moment. There is a simple reason for the asymmetry of the electronic distribution in HD^+. For deuterium, the reduced mass and binding energy are slightly larger, and the corresponding wave function smaller, than for hydrogen. This leads to the contribution of the ionic structure H^+D^- being slightly larger than that of H^-D^+, and in affect to a net moment $H^{+\delta}D^{-\delta}$. The values of $\langle r^2_{HD}\rangle$, $\langle r^2_{He}\rangle$, and $\langle r^2_{De}\rangle$ for the wave functions of different lengths are presented in Table VI and indicate that the electron shift toward the deuterium nucleus is correctly predicted in this approach.

VII. Newton–Raphson Optimization of Many-Body Wave Function

The recent remarkable progress in theoretical evaluation of structures and properties of molecular systems has been mainly due to the development of analytical derivative techniques. These techniques allow not only for very fast and effective determination of equilibrium geometries, but also allow optimizations of the nonlinear parameters involved in the basis functions. This represents the next important element in the development of our nonadiabatic methodology. The problem which arises in minimization of the variational functional, as indicated the last section summary, is the number of nonlinear parameters in the wave function which should be optimized. This number increases very rapidly with the length of the expansion and the optimization procedure becomes very expensive.

In our initial calculations we used a two-step optimization procedure. For a given basis set defined by the set of nonlinear parameters we solved the standard secular equation, $\mathbf{H}_{tot}\mathbf{C} = \mathbf{SCE}$, ($\mathbf{H}_{int}\mathbf{C} = \mathbf{SCE}$, in the case of method II) to determine the optimal linear coefficients. Then we used the numerical conjugate gradient method to find the optimal set of nonlinear parameters. In this section we will show how the analytically determined first and second derivatives of the variational functional with respect to the orbital and correlation exponents have been incorporated into our procedure.

Let $\mathbf{X}(x_1, x_2, ..., x_n)$ be the n-dimensional vector of nonlinear parameters, *i.e.*, both orbital and correlation exponents. The Taylor expansion of the variational functional about point $\mathbf{X}^*$ can be obtained as follows:

$$J[\mathbf{X};k] = J[\mathbf{X}^*;k] + \sum_{i=1}^{n} \frac{\partial J[\mathbf{X};k]}{\partial x_i}\Big|_{\mathbf{x}^*}(x_i - x_i^*) + \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n} \frac{\partial^2 J[\mathbf{X};k]}{\partial x_i \partial x_j}\Big|_{\mathbf{x}^*}(x_i - x_i^*)(x_j - x_j^*) + ... \quad (7.1)$$

or, in the matrix form (the expansion is truncated after the quadratic term)

$$J[\mathbf{X};k] = J[\mathbf{X}^*;k] + \nabla J[\mathbf{X};k]|^{\mathrm{T}}_{\mathbf{x}^*}(\mathbf{X} - \mathbf{X}^*) + \frac{1}{2}(\mathbf{X} - \mathbf{X}^*)^{\mathrm{T}}\mathbf{H}|_{\mathbf{x}^*}(\mathbf{X} - \mathbf{X}^*) \quad (7.2)$$

where $\mathbf{H}|_{\mathbf{x}^*}$ denotes the Hessian evaluated at the $\mathbf{X}^*$ point. At a stationary point the gradient becomes equal to zero, $\nabla J[\mathbf{X};k]|^{\mathrm{T}}_{\mathbf{x}^*} = 0$. If the expansion (eq 2.11) is dominated by the linear and quadratic terms and the Hessian matrix is positive defined, then one can use the approximate quadratic expression to find the minimum of the functional (Newton–Raphson method):

$$\mathbf{X}_{min} = -(\mathbf{H}(\mathbf{X})|_{\mathbf{x}^*})^{-1}(\nabla J[\mathbf{X};k]|_{\mathbf{x}^*}) \quad (7.3)$$

Let us consider the first and second derivatives of the functional $J[\{\alpha_p\},\{\beta_{pq}\};k]$ with respect to an arbitrary parameter ξ. The first derivative is formulated as

$$\frac{\partial}{\partial\xi}J[\{\alpha_p\},\{\beta_{pq}\};k] = \frac{1}{\langle\Psi|\Psi\rangle}\left[\frac{\partial}{\partial\xi}\langle\Psi|H|\Psi\rangle + k\frac{\partial}{\partial\xi}\langle\Psi|T_{CM}|\Psi\rangle\right] - J[\{\alpha_p^i\},\{\beta_{pq}^i\};k]\frac{1}{\langle\Psi|\Psi\rangle}\frac{\partial}{\partial\xi}\langle\Psi|\Psi\rangle \quad (7.4)$$

where ξ can be α_p^i or β_{pq}^i. The second derivative of energy with respect to ξ and ζ can be obtained in a similar way

$$\frac{\partial^2}{\partial\zeta\partial\xi}J[\{\alpha_p\},\{\beta_{pq}\};k] = \frac{1}{\langle\Psi|\Psi\rangle}\left[\frac{\partial^2}{\partial\zeta\partial\xi}\langle\Psi|H|\Psi\rangle + k\frac{\partial^2}{\partial\zeta\partial\xi}\langle\Psi|T_{CM}|\Psi\rangle\right] - \frac{1}{\langle\Psi|\Psi\rangle}\left(\frac{\partial}{\partial\zeta}\langle\Psi|\Psi\rangle\right)\left(\frac{\partial}{\partial\xi}J[\{\alpha_p^i\},\{\beta_{pq}^i\};k]\right) - \frac{1}{\langle\Psi|\Psi\rangle}\left(\frac{\partial}{\partial\zeta}\langle\Psi|\Psi\rangle\right)\left(\frac{\partial}{\partial\zeta}J[\{\alpha_p^i\},\{\beta_{pq}^i\};k]\right) - J[\{\alpha_p^i\},\{\beta_{pq}^i\};k]\frac{1}{\langle\Psi|\Psi\rangle}\frac{\partial^2}{\partial\zeta\partial\xi}\langle\Psi|\Psi\rangle \quad (7.5)$$

As was mentioned above, the set of linear coefficients is obtained by solving the secular equation. In the case of the method I, this set is not optimal with respect to the variational functional J, because J contains an additional term $k\langle\Psi|T_{CM}|\Psi\rangle$ which is not present in the secular equation. However, the set becomes optimal if k is equal to zero, or when the kinetic energy of the center of mass motion vanishes. Therefore, the smaller the $\langle\Psi|T_{CM}|\Psi\rangle$ term is, the more fulfilled the condition

$$\frac{\partial}{\partial C_i}J[\{\alpha_p^i\},\{\beta_{pq}^i\};k] = 0 \quad (7.6)$$

should become.

In method II the solution of the secular equation implies that the above equation (eq 7.6) is exactly satisfied at each step of the minimization process. To make the above equations more explicit let us consider matrix elements with the function given previously

$$\langle\Psi|\hat{O}|\Psi\rangle = \sum_{l=1}^{M}\sum_{k=1}^{M} C_l C_k \langle P[\omega_l\Theta_{S,M}^N]|\hat{O}|\omega_k\Theta_{S,M}^N\rangle \quad (7.7)$$

where $\hat{O} = H_{tot}$, T_{CM}, or 1. The derivative with respect to ξ^k is

$$\frac{\partial}{\partial\xi^k}\langle\Psi|\hat{O}|\Psi\rangle = \sum_{l=1}^{M}(1 + \delta_{lk})C_l C_k\left\langle P[\omega_l\Theta_{S,M}^N]\middle|\hat{O}\middle|\frac{\partial}{\partial\xi^k}\omega_k\Theta_{S,M}^N\right\rangle \quad (7.8)$$

where we assumed that the linear coefficients are fixed and their derivatives with respect to Gaussian exponents are zero (this is exactly satisfied in method II). The second derivative of $\langle\Psi|\hat{O}|\Psi\rangle$ with respect to ζ^l when $l \neq k$ is

$$\frac{\partial^2}{\partial\zeta^l\partial\xi^k}\langle\Psi|\hat{O}|\Psi\rangle = (1 + \delta_{lk})C_l C_k\left\langle P\left[\frac{\partial}{\partial\zeta^l}\omega_l\Theta_{S,M}^N\right]\middle|\hat{O}\middle|\frac{\partial}{\partial\xi^k}\omega_k\Theta_{S,M}^N\right\rangle \quad (7.9a)$$

and when $l = k$,

$$\frac{\partial^2}{\partial\zeta^k\partial\xi^k}\langle\Psi|\hat{O}|\Psi\rangle = (1 + \delta_{lk})C_l C_k\left\langle P[\omega_l\Theta_{S,M}^N]\middle|\hat{O}\middle|\frac{\partial^2}{\partial\zeta^k\partial\xi^k}\omega_k\Theta_{S,M}^N\right\rangle + 2C_k^2\left\langle P\left[\frac{\partial}{\partial\zeta^k}\omega_l\Theta_{S,M}^N\right]\middle|\hat{O}\middle|\frac{\partial}{\partial\xi^k}\omega_k\Theta_{S,M}^N\right\rangle \quad (7.9b)$$

For the first derivative one needs to consider two cases: the first derivative with respect to an orbital exponent and with respect to a correlation exponent. For the second derivative one needs to consider three cases. The first one corresponds to the second derivative with respect to two orbital exponents. The second is the case of a mixed derivative with respect to orbital and correlation exponents. The third is the derivative with respect to two correlation exponents. For some integrals these three categories do not exhaust all the possibilities and some more specific cases need to be considered. Details of the evaluation of those special cases can be found in our previous study.[85,86]

As an example let us consider the overlap integral

$$\langle\omega_l(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)|\omega_k(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)\rangle = \pi^{3N/2}[\det(\mathbf{A}^{lk} + \mathbf{B}^{lk})]^{-3/2} \quad (7.10)$$

The first derivative with respect to ξ representing an orbital or correlation exponent is

$$\frac{\partial}{\partial\xi}\langle\omega_l|\omega_k\rangle = -\frac{3}{2}\pi^{-N}\langle\omega_l|\omega_k\rangle^{5/3}\frac{\partial}{\partial\xi}\det(\mathbf{A}^{lk} + \mathbf{B}^{lk}) \quad (7.11)$$

The second derivative with respect to ζ and ξ can be calculated in a similar way as the first derivatives.

$$\frac{\partial^2}{\partial\zeta\partial\xi}\langle\omega_l|\omega_k\rangle = \frac{15}{4}\pi^{-2N}\langle\omega_l|\omega_k\rangle^{7/3}\left[\frac{\partial}{\partial\zeta}\det(\mathbf{A}^{lk} + \mathbf{B}^{lk})\right]\left[\frac{\partial}{\partial\xi}\det(\mathbf{A}^{lk} + \mathbf{B}^{lk})\right] - \frac{3}{2}\pi^{-N}\langle\omega_l|\omega_k\rangle^{5/3}\frac{\partial^2}{\partial\zeta\partial\xi}\det(\mathbf{A}^{lk} + \mathbf{B}^{lk}) \quad (7.12)$$

Since

$$\left(\frac{\partial}{\partial\zeta}\langle\omega_l|\omega_k\rangle\right)\left(\frac{\partial}{\partial\xi}\langle\omega_l|\omega_k\rangle\right) = \frac{9}{4}\pi^{-2N}\langle\omega_l|\omega_k\rangle^{-10/3}\left[\frac{\partial}{\partial\zeta}\det(\mathbf{A}^{lk} + \mathbf{B}^{lk})\right]\times\left[\frac{\partial}{\partial\xi}\det(\mathbf{A}^{lk} + \mathbf{B}^{lk})\right] \quad (7.13)$$

the derivative can be simplified as

$$\frac{\partial^2}{\partial\zeta\partial\xi}\langle\omega_l|_k\rangle = \frac{5}{3}\langle\omega_l|\omega_k\rangle^{-1}\left(\frac{\partial}{\partial\zeta}\langle\omega_l|\omega_k\rangle\right)\left(\frac{\partial}{\partial\xi}\langle\omega_l|\omega_k\rangle\right) - \frac{3}{2}\pi^{-N}\langle\omega_l|\omega_k\rangle^{5/3}\frac{\partial^2}{\partial\zeta\partial\xi}\det(\mathbf{A}^{lk} + \mathbf{B}^{lk}) \quad (7.14)$$

The above formula has an interesting feature. Notice that the second derivative is expressed in terms of the overlap integral, its first derivatives, and the second derivative of the determinant det $(\mathbf{A}^{lk} + \mathbf{B}^{lk})$ which contains orbital and correlation exponents. The second derivatives of other integrals have a similar structure. This facilitates an efficient and transparent computer implementation of the derivative algorithms that has been accomplished recently.[86]

To illustrate the performance of the optimization method on the first and second analytical derivatives, we performed variational nonadiabatic calculations on the HD^+ molecule. For this system we used the following variational wave function:

$$\Psi_{tot} = \sum_{k=1}^{M} c_k\omega_k(\mathbf{r}_D, \mathbf{r}_H, \mathbf{r}_e)\Theta(D)\Theta(H)\Theta(e) \quad (7.15)$$

with the spatial part

$$\omega_k = \exp[-(\mathbf{r}_D, \mathbf{r}_H, \mathbf{r}_e)(\mathbf{A}^k + \mathbf{B}^k)(\mathbf{r}_D, \mathbf{r}_H, \mathbf{r}_e)^T] \quad (7.16)$$

In eq 7.14, $\Theta(D)$, $\Theta(H)$, and $\Theta(e)$ are spin functions for the deuteron, proton, and electron respectively. We assumed that spin coupling between particles is negligible. The HD^+ wave function does not possess any permutational symmetry with respect to exchange of particles. In our study we performed calculations with different number of Gaussian basis functions. The values of internal energies obtained using Newton–Raphson optimization technique are the same as the ones from numerical optimization, however they are obtained much faster.

Upon examining the data one can see good convergence of the results to the best literature value of −0.597 897 967 au.[43] The calculations on HD^+ have shown that the Newton–Raphson procedure is significantly faster and more efficient than the numerical optimization.

The above presented theory of first and second analytical derivative represents an important development in practical implementation of our nonadiabatic methodology. The optimization procedure based on analytical derivatives facilitates relatively fast calculations with long basis function expansions.

VIII. Future Directions

The presented review of nonadiabatic approaches for molecules shows that the level of complexity in calculations grows dramatically when the number of particles increases. In our nonadiabatic approach we accomplished some simplification of the many-body nonadiabatic problem by retaining the Cartesian coordinate frame rather than transformation of the problem to the CM coordinate frame. In this approach we gain a unique insight into the quantum state of the molecule without making any approximations with regard to the separability of the nuclear and electronic motions.

The nonadiabatic corrections are usually very small for molecular systems and exceptions are rare. A meaningful nonadiabatic calculation should be very accurate. By undertaking the effort of developing the "technology" of Gaussian cluster functions for nonadiabatic calculations, we believe that we can accomplish the required level of accuracy and successfully extend the nonadiabatic treatment beyond three-particle systems. One of the most important directions seems to be derivation and implementation of the first- and second-order derivatives of Gaussian cluster functions with respect to exponential parameters. The preliminary results are encouraging. The algorithm of the method based on the Newton–Raphson optimization scheme and analytical derivatives is very well suited for a parallel computer system and such an implementation will be pursued.

Several "even tempering" procedures exist for generating Gaussian orbital exponents and there are a few for generating Gaussian correlation exponents for correlated electronic wave functions. An even-tempered procedure is also possible in our approach; however, the situation here is significantly more complicated due to the fact that the particles presented by the correlated wave function can have different masses and charges. The development of an even-tempered procedure will allow us to greatly reduce the expense of the parameter optimization effort and, in consequence, will allow treatment of larger systems.

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