Non-Born–Oppenheimer variational calculations of HT$^+$ bound states with zero angular momentum

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We report fully nonadiabatic calculations of all rotationless bound states of HT$^+$ molecular ion ($t^+p^+e^-$) carried out in the framework of the variational method. We show that, in all the states, except the two highest ones, the bond in the system can be described as covalent. In the highest two states the bond becomes essentially ionic and HT$^+$ can be described as a T$^+$H$^+$ complex. The wave function of the system was expanded in terms of spherically symmetric, explicitly correlated Gaussian functions with preexponential multipliers consisting of powers of the internuclear distance. Apart from the total energies of the states, we have calculated the expectation values of the $r$-p, $r$-e, and p-e interparticle distances, their squares, and the nucleus-nucleus correlation functions. © 2005 American Institute of Physics. [DOI: 10.1063/1.1884602]

I. INTRODUCTION

The HD$^+$ molecular ion has been a model system for studies of the nonadiabatic coupling between the electronic and nuclear motions. The lack of a center of symmetry in this system due to different nuclear masses requires that the theoretical approach for calculating its stationary bound states is somewhat different than that applied to the parent symmetric cation, H$_4^+$, where an obvious placement of the center of the internal coordinate system is the middle of the bond. Since the HT$^+$ has even larger nuclear mass difference than HD$^+$, the approach applied to both systems may be similar. While the asymmetry of the HD$^+$ system has been extensively investigated both experimentally$^{1–3}$ and theoretically,$^{4–6}$ including our recent work,$^7$ there have been only a few studies (only theoretical) concerning the HT$^+$ molecular ion.$^8–10$

In a recent work Ben-Itzhak et al.$^7$ studied the dissociation of the electronic ground state of HD$^+$ following ionization of HD by fast proton impact and discovered that the H$^+$+D(1s) dissociation channel is more likely than the H(1s)+D$^+$ channel by about 7%. This symmetry breakdown can only be explained if the finite nuclear mass correction to the Born–Oppenheimer (BO) approximation is taken into account. In our non-BO calculation,$^7$ we showed that while in the first 21 vibrational states ($v=1,2,\ldots,20$) only minor charge asymmetry is present in the wave functions, in the highest two states ($v=21$ and $v=22$) HD$^+$ is strongly polarized and the system can be described as a complex of D and H$^+$ (D+H$^+$ is also the lowest energy dissociation product of the HD$^+$ ion).

In this work we consider the charge asymmetry of the HT$^+$ ion. 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 this work will 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.$^9,10$

If the starting point of considering the HT$^+$ ion is its representation based on the BO approximation, the charge asymmetry in the system appears as a nonadiabatic coupling between the gerade and ungerade electronic states. The two states mix due to the coupling of the nuclear and electronic motions. The coupling increases near the dissociation limit where the dissociation energy becomes comparable to the total energy difference of H and T atom ground states.

The T atom is energetically more stable than H because it has slightly larger reduced mass, which makes the average electron-nucleus distance slightly shorter in T than in H resulting in stronger coulombic attraction and lower energy. Thus, upon dissociation, HT$^+$ splits into T+H$^+$ which is a lower-energy dissociation product than T$^+$+H. There are two previous theoretical works concerning HT$^+$ that need to be mentioned. Bishop et al.$^8$ and Bishop and Cheung$^9$ first applied an approach to HT$^+$ that did not involve the adiabatic approximation and was based on the variational principle. They calculated the ground and the first two excited vibrational states, as well as a few lowest rotational states of the ion. Most recently, Frolov$^{10}$ applied a fully nonadiabatic variational approach using exponential basis function with complex parameters to refine the total ground-state energies for...
the heteronuclear and homonuclear isotopomers of $H_2^+$, including $HT^*$. In this work we compare our energy results with those of Bishop and Cheung, and of Frolov.

In the present work, we use the approach we have developed to perform rigorous ground-state and excited state non-BO calculations on diatomic systems with an arbitrary number of electrons. The approach is based on separating the operator describing the center of mass kinetic energy from the total Hamiltonian of the system and representing the remaining internal Hamiltonian in the reference frame centered at one of the particles (in most cases the heaviest particle). In the calculation we use the explicitly correlated $n$-particle Gaussian functions to expand the spatial part of the wave function. No approximation is made in the approach apart from neglecting the relativistic effects and using a finite basis set expansion of the wave function. As we have demonstrated on a number of cases, including, for example, the $H_2$ molecule, and most recently the HD$^+$ ion, the approach produces very accurate results.

Since the vibrational quantum number is not a “good” quantum number in the non-BO calculation (only the values of the square of the total, i.e., electronic plus nuclear, angular momentum and its projection on a selected axis are good quantum numbers) we need to explain what we mean by the term “vibrational spectrum.” Our use of the term refers to the ground and excited states with certain value of the total angular momentum. In the present calculations this has been the ground rotational state (i.e., the state with zero total angular momentum; the rotationless state).

In this work, we have also calculated the expectation values of all interparticle distances (i.e., $r_{p,i}$, $r_{p,ei}$, and $r_{pe}$) and their squares for all considered states. The algorithm for calculating these quantities is shown in the Appendix. The comparison of the $(r_{pe})$ and $(r_{p,ei})$ has allowed us to examine the charge asymmetry that occurs in $HT^*$. To our knowledge, this is the first direct calculation of these quantities for this system that uses rigorous nonadiabatic wave functions.

Although the present calculations have concerned the whole rotationless $HT^*$ spectrum, our main focus was the highest few vibrational states where the most significant charge asymmetry is expected to occur. Thus, while all the states have been calculated with very high precision, in the highest two states the number of basis function was significantly increased to improve the precision even further. Not only this generated better energy values for those states, but also allowed to examine the convergence of the procedure in terms of the number of the basis functions in the wave function expansion. Since the wave functions of the highest two states contain the largest number of radial nodes, these states were the most difficult to describe. The analysis of the convergence of the energy and the averaged interparticle distances performed for the two states show how reliable the calculations are not only for those states, but also for the other states where, due to fewer radial nodes, the basis set size did not have to be as large.

**II. THE HAMILTONIAN**

In the approach we use, we begin with the total nonrelativistic Hamiltonian for a molecular system in the laboratory Cartesian coordinates. All particles present in the system are included in the Hamiltonian. For $HT^*$ it looks as follows (in atomic units):

$$\hat{H}_{\text{TOT}} = -\sum_{i=1}^{3} \frac{1}{2M_i} \nabla_i^2 + \sum_{i>j=1}^{3} \frac{Q_i Q_j}{R_{ij}},$$

where $M_i$, $Q_i$, and $R_{ij}$ are the masses, the charges, and the position vectors of the tritium nucleus, the proton, and the electron respectively ($M_1 = m_e$, $M_2 = m_p$, $M_3 = m_e$, $Q_1 = 1$, $Q_2 = 1$, $Q_3 = -1$), and where $R_{ij} = |\mathbf{R}_i - \mathbf{R}_j|$ are interparticle distances. Note that no distinction between the electron and the nuclei is made and the two types of particles are treated equivalently. In the next step, we transform the laboratory coordinate system to a new coordinate system, whose first three coordinates are the Cartesian coordinates describing the position of the center of mass in the laboratory coordinate system and the remaining six coordinates are internal coordinates. The internal coordinates are defined with respect to a Cartesian coordinate system whose origin is placed at the tritium nucleus and whose axes are parallel to the axes of the laboratory coordinate frame. The three first of the six internal coordinates, $r_1 = |\mathbf{R}_1 - \mathbf{R}_2|$, describe the position of the proton with respect to the coordinate origin and the last three, $r_2 = |\mathbf{R}_3 - \mathbf{R}_1|$, describe the position of the electron. Using the new coordinates, we can separate the Hamiltonian representing the motion of the center of mass in the laboratory coordinate system from the internal Hamiltonian, $\hat{H}_{\text{INT}} = \hat{H}$, thereby reducing the three-particle problem to a two-pseudoparticle problem. The internal Hamiltonian has the following form:

$$\hat{H} = \frac{1}{2} \left( \sum_{i=1}^{2} \frac{1}{m_i} \nabla_i^2 + \sum_{i+j=1}^{2} \frac{1}{M_1} \nabla_i^2 \nabla_j^2 \right) + \sum_{i=1}^{2} \frac{q_0 q_i}{r_i} + \sum_{i<j} \frac{q_i q_j}{r_{ij}}.$$  

This Hamiltonian describes a system containing the reference particle (triton) at the origin of the coordinates with charge $q_0 = Q_1 = 1$ and two pseudoparticles, or internal particles, with reduced masses $m_1 = m_e m_p / (m_e + m_p)$ and $m_2 = m_e m_p / (m_e + m_p)$, and charges $q_1 = 1$ and $q_2 = -1$. Thus, the wave function describing the internal motion of the system, $\Psi(r_1, r_2)$, is dependent on the Cartesian coordinates of two pseudoparticles, the first resembling the proton and the second resembling the electron. The second term in the parenthesis in Eq. (2) is the mass polarization term, which arises from the coordinate transformation and which couples the motion of the two pseudoparticles. In the potential energy term, $r_i$ and $r_{ij}$ are defined as $r_i = |\mathbf{r}_i| = |\mathbf{R}_{i+1} - \mathbf{R}_1|$ and $r_{ij} = |\mathbf{R}_{i+1} - \mathbf{R}_{i+1}| = |\mathbf{r}_i - \mathbf{r}_j|$.

Since the mass of the pseudoproton is much larger than the mass of the pseudoelectron, all lower bound states of the system correspond to excitations (either “rotational” or “vibrational”) of the nuclear motion. In particular, as mentioned before, if the calculation is restricted only to rotationless states (i.e., fully spherically symmetric states), only the vibrational states are obtained. In those states, higher excitation should generate larger numbers of radial nodes in the wave function in terms of the pseudoproton coordinates.
Another important feature of the eigenfunctions of the Hamiltonian (2), which does not appear in the electronic states, results from the repulsion of the pseudoproton with the positive charge at the coordinate origin. Due to the repulsion, the wave function should significantly decrease in magnitude when the distance of the pseudoproton to the origin shortens. For bound states the wave function should also become smaller for larger distances. In between, the vibrational wave function should reach a maximum (near the equilibrium internuclear distance for the considered state) and, depending on the excitation level, it should have several radial oscillations. The basis set used in the calculation should be capable of describing these features very accurately.

III. THE WAVE FUNCTION

In our previous works, we have shown that the explicitly correlated Gaussian basis set involving functions with preexponential multipliers consisting of the internuclear distance \( r_1 \) raised to a non-negative even power \( m \) (Refs. 12 and 13)

\[
\psi_i = r_1^m \exp\left[ -r \left( A_k \otimes I_3 \right) r \right]
\]

(3)
is capable of very effectively describing nonadiabatic zero angular momentum states of diatomic systems with \( \sigma \) electrons. In those functions, the combination of the preexponential powers of the internuclear distance and the Gaussian exponents dependent on the coordinates of all pseudoparticles and their relative distances describes very effectively the correlated motion of the pseudonucleus and the pseudoelectrons in the central potential of the positive charge located at the origin of the coordinate system. The exponential coefficients in the Gaussian (3) form the symmetric matrix \( A_k \). In our calculations, this matrix is expressed as a product of an \( n \times n \) lower triangular matrix \( L_k \) of rank \( n \) and its transpose, \( L_k^T \). This is done to avoid dealing with constraints that would need to be imposed on the elements of the matrix \( A_k \) due to the required square integrability of functions (3) in the optimizations of the \( A_k \) matrix elements. With the use of the \( L_k L_k^T \) decomposition of \( A_k \), the square integrability is automatically satisfied for any variation of the elements of \( L_k \) in the range \( [-\infty, \infty] \). In Eq. (3), \( I_3 \) is the \( 3 \times 3 \) identity matrix, and in general, \( I_n \) is the \( n \times n \) identity matrix, \( \otimes \) denotes the Kronecker Product, and \( r \) is a \( 3n \times 1 \) vector of the internal Cartesian coordinates \( r \) of the \( n \) pseudoparticles. The fact that functions (3) correspond to zero total angular momentum follows from their rotational invariance.11

In the HT\(^+\) calculations, the spin free wave functions, \( \Psi(r) = \sum \psi_i(r_1, r_2) \), for all rotationless states have been generated as expansions in terms of two-particle Gaussians of the form given by the expression (3):

\[
\psi_i = \sum_{k=1}^{K} c_k \phi_k(r).
\]

(4)
The powers \( m_k \) ranged from 0 to 250 in the calculations. This rather extended range of powers was needed to accurately represent oscillations of the vibrational part of the wave functions which are particularly strong in highly excited states.

IV. THE VARIATIONAL CALCULATIONS

The ground-state and excited state nonadiabatic wave functions for HT\(^+\) in the present calculations were obtained by minimizing the Rayleigh quotient:

\[
E(\{c_j\}, \{m_j\}, \{L_k\}) = \min_{\{c_j\}, \{m_j\}, \{L_k\}} \sum_{\{c_j\}, \{m_j\}, \{L_k\}} c_j^* H(\{m_j\}, \{L_k\}) c_j
\]

with respect to the basis function exponential parameters \( \{L_k\} \) and the preexponential powers \( \{m_j\} \). The minimum with respect to the expansion coefficients of the wave function in terms of the basis functions \( c_j \) was found by solving the secular equation.

Much of the recent progress in the area of very accurate non-BO diatomic calculations has been due to the derivation and implementation of analytical gradients of the energy functional (5) with respect to variational nonlinear parameters of the basis functions. In the minimization of the energy functional, the availability of the analytical gradient of the energy leads to significant acceleration of the optimization process and allows one to apply the procedure to functionals dependent on hundreds or even thousands of variational parameters.

To achieve the best results in the parameter optimization with the least computational effort, we have recently implemented a hybrid approach that combines the gradient based optimization with the stochastic selection method.16,17 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. To reach high accuracy in the 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. Having the energy determined with several basis set expansion lengths for the highest two states allowed analysis of the convergence of the procedure in terms of the number of basis functions. The calculations have been carried out at the University of Arizona Center of Computing and Information Technology with the use of an HP Alpha GS1280 supercomputer.

After the wave functions for all 24 \( (v=0, \ldots, 23) \) states were generated, we calculated the expectation values of the internuclear triton–proton distance, \( (r_{tp}) \), the triton–electron \( (t-e) \) distance, \( (r_{te}) \), and the proton–electron \( (p-e) \) distance, \( (r_{pe}) \), for each state. We also calculated the average values of the squares of the distances. The derivation of the formula for calculating the expectation values is given in the Appendix. In our calculations, we used the following values for the nuclear masses: \( m = 5496.921 503 m_e \), where \( m_e \) stands for

the mass of the electron $m_p = 1836.15267261m_e$. These values were taken from CODATA 2002 (Ref. 20) list of fundamental constants.

### V. RESULTS AND DISCUSSION

In Table I we compare our variational energy values for the $v=0$–23 states of HT$^+$ with the energy values of some states available in the literature. In the same table we also show the expectation values of the interparticle distances and their squares obtained in the calculations. As one could expect, the average internuclear distance increases with the rising level of excitation. This increase becomes more pronounced as the excitation level approaches the dissociation threshold. For $v=21$, $v=22$, and $v=23$ states (the highest levels corresponding to a bound state) the average internuclear distance increases from 8.139 a.u. to 11.11 a.u., and then to 19.91 a.u. respectively. In the $v=23$ state, the HT$^+$ ion is only bound by $8 \times 10^{-6}$ hartree and the system is almost dissociated.

Our HD$^+$ calculations demonstrated\(^7\) that system becomes essentially ionic in the last two rotationless vibrational states. As the results in Table I show, the same effect occurs in the HT$^+$ ion, though the charge asymmetry in the highest state is somewhat lower than that in the highest state of HD$^+$. In this highest state of HT$^+$ the $t\cdot e$ average distance is 1.729 a.u., while the $p\cdot e$ distance is 19.72 a.u. Due to this high asymmetry the HT$^+$ bond in this state can be described as ionic. In the lower states, as it was the case with the HD$^+$ ion, some charge asymmetry is also present in the $t\cdot e$ and $p\cdot e$ distances and this asymmetry progressively increases with the increasing excitation level. However, the HT$^+$ bond in the $v=0$–21 states can still be described as mostly covalent.

To illustrate the convergence of the energy and the expectation values of the interparticle distances, we show in Table II the results for the ground ($v=0$) and for the highest two states ($v=22$ and 23) obtained with different basis sizes ranging from 500 to 5000. The two highest states are the most difficult to describe due to the highest number of radial nodes in their wave functions and due to their significant spatial diffuseness. The results presented in Table II show that both the energy and the distances converged quite well. With 1500 functions in the basis for the ground state, the energy is converged in nine significant figures. For the highest states the number of converged figures is 8. One may expect that to reach a similar convergence level for all states one needs to progressively increase the number of basis functions going from the bottom to the top of the spectrum. This is what has been done in the present calculations as shown by the number of functions used for each state shown in the second column in Table I. However, as the Gaussians are usually less effective in describing the electronic and nuclear cusps than the other regions of the wave function, there may be some residual error left in our energies. Our

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**Table I.** Total energies, expectation values of the triton-proton distance, $r_{tp}$, the triton-electron distance, $r_{te}$, and the proton-electron distance, $r_{pe}$, and their squares for the rotationless bound states of HT$^+$. All quantities are in atomic units. $K$ is the number of basis functions.

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<th>$\langle r_{te} \rangle$</th>
<th>$\langle r_{pe} \rangle$</th>
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\(^{a}\)Obtained with the following mass ratios: $m_t/m_p = 0.000$ 544 617, $m_p/m_e = 0.000$ 181 920.

\(^{b}\)Obtained with $m_t = 1836.152$ 701$m_e$, $m_p = 5496.921$ 58$m_e$.

\(^{c}\)T atom in the ground state.
TABLE II. The convergence of the energy and the expectation values of the interparticle distances for the \( v=22 \) and 23 states with the number of the basis functions. All quantities in atomic units.

<table>
<thead>
<tr>
<th>Basis size</th>
<th>( E )</th>
<th>( \langle r_{pp} \rangle )</th>
<th>( \langle r_{pe} \rangle )</th>
<th>( \langle r_{pe} \rangle )</th>
<th>( \langle r_{pp}^2 \rangle )</th>
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<td>1.685 83</td>
<td>1.686 77</td>
<td>4.251 88</td>
<td>3.524 75</td>
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<tr>
<td>( v=22 )</td>
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</tr>
</tbody>
</table>

estimation for that error in the \( v=22 \) state of HD\(^+\) with 4000 terms in the basis was about \( 10^{-9} \) hartree (see Table II in Ref. 7). An error of the same order of magnitude is probably also present in our 5000–term energy results for the \( v=22 \) and 23 states of HT\(^+\).

The lower effectiveness of Gaussians in describing the cusps is also likely to be partially responsible for the difference between our ground state energy and the value recently reported by Frolov,\(^{10}\) who used complex exponential basis functions, and shown in Table I. 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.

In our recent work\(^{21}\) we developed an algorithm to calculate and plot the pseudonucleus density (or, as it can be also called, the nucleus-nucleus correlation function) based on the wave function obtained in the non-BO calculation. The pseudonucleus density is defined as

\[
g(\xi) = \langle \Psi(\mathbf{r}) | \delta(\mathbf{r}_1 - \xi) | \Psi(\mathbf{r}) \rangle = \int |\Psi(\xi, \mathbf{r}_2)|^2 d\mathbf{r}_2. \tag{6}
\]

The algorithm has been applied in this work to show the pseudoproton density for different states of the HT\(^+\) ion. In Figs. 1 and 2 we show the pseudoproton densities in the two-dimensional (2D) and 3D forms for a few states from the bottom, middle, and the top of the spectrum. We included both 2D and 3D plots because, while the former better show the radial behavior of the pseudonucleus density, the latter better demonstrate the spherical radial symmetry of this quantity. In the highest, \( v=23 \) state, the wave function and, thus, the density have 23 radial nodes. Judging from the energy values, the Gaussian basis set we use is capable of describing this very complicated nodal structure very well. One might be somewhat surprised by the fact that in Fig. 1 for the \( v=23 \) state the curve does not touch the \( \xi \) axis before the last oscillation (see the enlarged fragment of the plot).

Our interpretation of this effect is the following. In the non-Born–Oppenheimer calculation the wave function describes simultaneous motion of nuclei and electrons (or, as should be more correctly described, the motion of pseudonuclei and pseudoelectrons). Obviously, the wave function for the highest state has to be orthogonal to the wave functions of all lower states. For rotationless states this orthogonality can be achieved by the wave function for the highest state having the highest number of radial nodes. As mentioned before, the radial nodes can appear in the wave function for HT\(^+\) in terms of the pseudoproton coordinate \( r_1 \) but one can-
not exclude a possibility that, especially for the highest states, there may be a component in the wave function with a node in the pseudoelectron coordinate $r_2$. If this is the case the density for the $v=23$ state will be a sum of two contributions, one with 23 nodes in terms of $r_1$ and the second one with a node in terms of $r_2$ and fewer nodes (or even no nodes) in terms of $r_1$. This is a possible explanation of why we see some upshift of the density function away from the $\xi$ axis at the last node for the $v=23$ state. If this explanation is correct, the effect is purely nonadiabatic because it results from mixing of two electronic states.

VI. SUMMARY

In this work, rigorous, variational, high accuracy, nonadiabatic calculations employing explicitly correlated Gaussian basis functions have been performed for the HT$^+$ ion to determine its complete vibrational spectrum corresponding to zero rotational quantum number. This is the first work reporting non-BO energies for all the vibrational states of this system. The wave functions obtained in the calculations were used to determine expectation values of the $t$-$p$, $t$-$e$, and $p$-$e$ distances. Those values showed 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$^+$ and proton. 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.
ACKNOWLEDGMENTS

This work was partially supported by an international grant from the National Science Foundation. The work of E.B. on this project was supported by a grant from NASA.

APPENDIX: STRUCTURAL INTEGRALS

First, let us recall some definitions and theorems concerning matrix properties, which we will use in the derivation of the distance matrix elements.

The Taylor expansion has the form

\[ f(x) = \sum_{i=0}^{\infty} \frac{f^{(n)}(x_0)}{n!} (x - x_0)^n. \]  

(A1)

The Pochhammer symbol is defined as

\[ (a)_n = \prod_{k=0}^{n-1} (a + k) = \frac{\Gamma[a+n]}{\Gamma[a]}, \]  

(A2)

where \((a)_0 = 1\), and \(\Gamma[x]\) is the Euler gamma function.

We will use the Leibniz formula to determine the Nth derivative of the product of functions \(f\) and \(g\):

\[ (f \circ g)^{(N)} = \sum_{k=0}^{N} \binom{N}{k} f^{(N-k)} g^{(k)}. \]  

(A3)

Also, we will use a rank one \(J_{ij}\) matrix, which is defined as

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

where \(E_{ij}\) is the \(n \times n\) matrix with 1 in its \(i\)th position and 0’s elsewhere.

The basis functions, which have been used in our calculation have the form

\[ \langle \phi_i | = |r^{2m_i} e^{-\alpha_i^* \Delta t} | = |r^{2m_i} \phi_i |, \]  

(A4)

where \(\Delta t\) is a symmetric and positive definite matrix of nonlinear variational parameters. The notation \(\Delta_t\) denotes a Kronecker product of the \(\Delta_t\) matrix with the \(3 \times 3\) identity matrix, \(I_3\). Any integral with even power of interparticle distance \(r_{ij}^{2n}\) can be calculated using following expression:

\[ r_{ij}^{2n} = [ \alpha'(J_{kl} \otimes I_3)|^n \]  

(A5)

In particular, if \(s = t = 1\), \(r_{ij}^{2n}\) can be generated as

\[ r_{ij}^{2n} = [ \alpha'(J_{kl} \otimes I_3)|^n \]  

Any integrals with odd power of premultipliers \(r_{ij}^{2n-1}\) can be found by using the following integral representation of \(r_{ij}^{2n-1}\):

\[ r_{ij}^{2n-1} = \frac{2}{\sqrt{\pi}} \int_0^\infty dx e^{-x^2} J_{kl} |. \]  

(A6)

The expression for the overlap integral of basis functions \((A4)\) is well known and has the following form:

\[ \langle \phi_i | \phi_j \rangle = (\phi_i |(3/2)_{m_j+m_i}| \frac{1}{2} c_1 c_2 \rangle \]  

(A7)

where \(\langle \phi_i | \phi_j \rangle = \frac{1}{2} c_1 c_2 \rangle \) is the elemental overlap integral, and \(A^{1/2}_1\) is the inverse matrix. Vertical bars applied to a matrix denote the determinant of the matrix.

In order to evaluate the structural integrals, we combine some useful matrix properties into two theorems. Theorem A.1 can be found in Ref. 22 and Theorem A.2 has been taken from Ref. 23.

**Theorem A.1.** Let \(A\) and \(B\) be \(n \times n\) matrices. Then

\[ |A \otimes B| = |A|^n |B|^n, \]  

\[ \text{Tr}[A + B] = \text{Tr}[A] + \text{Tr}[B]. \]

**Theorem A.2.** Let \(G\) and \(G + H\) be nonsingular matrices with \(H = \sum_{i=1}^{N} H_i, C_i = G, C^{-1}_i = C^{-1}_i - v_i C^{-1}_i H C^{-1}_i, \) \(v_i^{-1} = 1 + \text{Tr}[C^{-1}_i H_i] \) and let \(H_i\) be matrix of rank 1. Then

\[ |G + H| = |G| \prod_{i=1}^{N} v_i^{-1}. \]

Taking into account that any premultiplier in the structural integrals can be expressed in the exponential form [Eqs. (A5) and (A6)], and using Theorem A.1 and Theorem A.2, the structural integral in the general form for even and odd powers \(R_{ij} = \langle \phi_i | e^{\alpha_i^* \Delta t/2} | \phi_j \rangle, R_{ij} = \langle \phi_i | e^{\alpha_i^* \Delta t/2} | \phi_j \rangle\) can be reduced to a product of derivatives of the elemental overlap integral:
\[ \eta = (-1)^N \frac{\partial^N}{\partial \beta^N} \int_0^\infty dx \nu_1^{3/2} \frac{\partial^N}{\partial \beta^N} \int_0^\infty dx \left[ 1 + (x^2 + \beta) \text{Tr}[C_1^{-1} H_2] \right]^{-3/2} = (-1)^N \frac{\partial^N}{\partial \beta^N} \left[ \text{Tr}[C_1^{-1} H_2] \right]^{-1/2} \left( 1 + \beta \text{Tr}[C_1^{-1} H_2] \right) \]

Then, setting \( \beta = 0 \), expanding \( C_1^{-1} \), taking into account that \( C_1 = I_n \), and using Taylor expansion (A1) yields the following:

\[ \eta_{\beta=0} = N! \left( \text{Tr}[C_1^{-1} H_2] \right)^{N-1/2} = N! \left( \text{Tr}[H_2] - \nu_1 \alpha \text{Tr}[H_1 H_2] \right)^{N-1/2} = N! \left( \text{Tr}[H_2] \right)^{N-1/2} \sum_{k=0}^\infty \frac{(N-k+1/2)_k}{k!} \left( -\nu_1 \alpha \frac{\text{Tr}[H_1 H_2]}{\text{Tr}[H_2]} \right)^k. \]  

(A9)

Now, differentiating of \( \nu_1^{3/2} \alpha^k \) with respect to \( \alpha \) and recalling the Leibniz formula (A2) we obtain

\[ \frac{\partial^M \nu_1^{3/2} \alpha^k}{\partial \alpha^M} \bigg|_{\alpha=0} = \sum_{m=0}^M \binom{M}{m} \frac{\partial^m \alpha^k}{\partial \alpha^m} \frac{\partial^{M-m} \nu_1^{3/2}}{\partial \alpha^{M-m}} \bigg|_{\alpha=0} = \sum_{m=0}^M \binom{M}{m} k! \frac{\alpha^{k-m}}{(k-m)!} \left( 1 + \alpha \text{Tr}[H_1] \right)^{(k+3/2)} \frac{\partial^{M-m} \nu_1^{3/2}}{\partial \alpha^{M-m}} \bigg|_{\alpha=0} \]

\[ = \sum_{m=0}^M \binom{M}{m} \frac{k!}{(k-m)!} \left( k + \frac{3}{2} \right)^{M-m} \text{Tr}[H_1]^{M-m} \left( 1 + \alpha \text{Tr}[H_1] \right)^{-(k+3/2+M-m)} \bigg|_{\alpha=0}. \]  

(A10)

Next, multiplying Eq. (A9) by \( \nu_1^{3/2} \), differentiating with respect to \( \alpha \), and applying (A10) gives

\[ \xi_{\alpha=0} = (-1)^M \frac{\partial^M \nu_1^{3/2} \eta_{\beta=0}}{\partial \alpha^M} \bigg|_{\alpha=0} = (-1)^MN! \left( \text{Tr}[H_2] \right)^{N-1/2} \sum_{k=0}^\infty \frac{(N-k+1/2)_k}{k!} \left( -\frac{\text{Tr}[H_1 H_2]}{\text{Tr}[H_2]} \right)^k \frac{\partial^M \nu_1^{3/2} \alpha^k}{\partial \alpha^M} \bigg|_{\alpha=0} \]

\[ = N! \left( \text{Tr}[H_1] \right)^M \left( \text{Tr}[H_2] \right)^{N-1/2} \sum_{k=0}^{\min(M,\infty)} \frac{(N-k+1/2)_k}{(M-k)!} \left( -\frac{\text{Tr}[H_1 H_2]}{\text{Tr}[H_2]} \right)^k \frac{\text{Tr}[H_1]^{M-k}}{\text{Tr}[H_2]^{M-k}}. \]  

(A11)

Finally, substituting Eq. (A11) into Eq. (A8) we find structural integral for odd power of \( r_{ij} \);
\[ R_s = \frac{2}{\sqrt{\pi}} \left( \phi_\alpha \phi_\beta \right) \Gamma \left[ M + \frac{3}{2} \right] (\text{Tr}[H_1])^M N! \left( \text{Tr}[H_2] \right)^{N-1/2} \sum_{k=0}^{M} \left( \Gamma \left[ N + \frac{1}{2} \right] \Gamma \left[ N - k + \frac{1}{2} \right] \left( \frac{\text{Tr}[H_1 H_2]}{\text{Tr}[H_1] \text{Tr}[H_2]} \right)^k \right) \]

\[ = \left( \phi_\alpha \phi_\beta \right) N! \left( \text{Tr}[H_2] \right)^{N-1/2} \sum_{k=0}^{M} \left( \Gamma \left[ N + \frac{1}{2} \right] \Gamma \left[ N - k + \frac{1}{2} \right] \left( \frac{\text{Tr}[H_1 H_2]}{\text{Tr}[H_1] \text{Tr}[H_2]} \right)^k \right) \]

\[ = \left( \phi_\alpha \phi_\beta \right) \left( \text{Tr}[H_2] \right)^{N-1/2} \frac{1}{\Gamma[3/2]} N! \left\{ \begin{array}{l} \frac{3}{2} \sqrt{N} \left( \frac{\text{Tr}[H_1 H_2]}{\text{Tr}[H_1] \text{Tr}[H_2]} \right)^{3/2} \end{array} \right\} . \quad (A12) \]

where \( _2F_1(a, b, c, x) \) is the hypergeometric function.

If we remove \( r_{ij}^{-1} \) from Eq. (A8) then we can get the formula for the structural integral with even powers in the following form:

\[ R_s = (-1)^{M+N} \left( \phi_\alpha \phi_\beta \right) \frac{\partial^M}{\partial \beta^M} \left[ \nu_1^{-1}(\alpha) \right]^{-3/2} \]

\[ \times \left. \frac{\partial^N}{\partial \alpha^N} \left[ \nu_2^{-1}(\beta, \alpha) \right]^{-3/2} \right|_{\alpha=\beta=0} . \quad (A13) \]

Applying the definition of \( \nu_2 \) from Theorem A.2, for the last term in Eq. (A13) we obtain

\[ \eta = (-1)^N \frac{\partial^N \left[ \nu_2^{-1}(\beta, \alpha) \right]^{-3/2}}{\partial \alpha^N} \]

\[ = \left. \frac{\partial (1 + \beta \text{Tr}[C_2^{-1} H_2])^{-3/2}}{\partial \beta^N} \right|_{\beta=0} \]

\[ = \left. \left( \frac{3}{2} \right)^{N} \frac{\text{Tr}[C_2^{-1} H_2]^N}{(\nu_2^{-1})^{N+3/2}} \right|_{\beta=0} \]

\[ = \left( \frac{3}{2} \right)^{N} \text{Tr}[C_2^{-1} H_2]^N . \quad (A14) \]

Now, multiplying \( \eta \) by the \( \lambda^{3/2} \), setting \( C_1 = I_n \), expanding \( \nu_1 \), results the following expression after simplification:

\[ \zeta = \nu_1^{3/2} \eta \left|_{\beta=0} \right. = \nu_1^{3/2} \left( \frac{3}{2} \right)^{N} \text{Tr}[C_2^{-1} H_2]^N \]

\[ = \left. \left( \frac{3}{2} \right)^{N} \nu_1^{3/2} (\text{Tr}[C_1^{-1} H_2] - \nu_1 \alpha \text{Tr}[C_1^{-1} H_1 C_1^{-1} H_2])^N \right|_{\beta=0} \]

\[ = \left. \left( \frac{3}{2} \right)^{N} \nu_1^{3/2} \left( \text{Tr}[H_2] - \nu_1 \alpha \text{Tr}[H_1 H_2] \right)^N = \left( \frac{3}{2} \right)^{N} \sum_{k=0}^{N} \left( \begin{array}{c} N \\ k \end{array} \right) \sum_{k=0}^{N} (\nu_1^{3/2} \left( \text{Tr}[H_2] - \nu_1 \alpha \text{Tr}[H_1 H_2] \right)^k (\frac{\text{Tr}[H_1 H_2]}{\text{Tr}[H_2]})^k \right)^{3/2} \]

\[ = \left. \left( \frac{3}{2} \right)^{N} \text{Tr}[H_2]^N \sum_{k=0}^{N} \left( \begin{array}{c} N \\ k \end{array} \right) (\frac{\text{Tr}[H_1 H_2]}{\text{Tr}[H_2]})^k \right)^{3/2} \]

\[ \times \alpha^k (1 + \alpha \text{Tr}[H_1])^{-3k/2} . \quad (A15) \]

Differentiating \( \zeta \) with respect to \( \alpha \) and recalling the Leibniz formula (A3) we have

\[ \xi_{\alpha=0} = (-1)^M \frac{\partial^M \zeta}{\partial \alpha^M} \]

\[ = (-1)^M \left( \frac{3}{2} \right)^{N} \text{Tr}[H_2]^N \sum_{k=0}^{N} \left( \frac{\text{Tr}[H_1 H_2]}{\text{Tr}[H_2]} \right)^k \sum_{m=0}^{M} \left( \begin{array}{c} M \\ m \end{array} \right) \left( \frac{\text{Tr}[H_1]}{\text{Tr}[H_2]} \right)^m \times \left( (1 + \alpha \text{Tr}[H_1])^{-k} \right) \]

\[ = (-1)^M \left( \frac{3}{2} \right)^{N} \text{Tr}[H_2]^N \sum_{k=0}^{N} \left( \frac{\text{Tr}[H_1 H_2]}{\text{Tr}[H_2]} \right)^k \sum_{m=0}^{M} \left( \begin{array}{c} M \\ m \end{array} \right) \left( \frac{\text{Tr}[H_1]}{\text{Tr}[H_2]} \right)^m \]

\[ \times (1 + \alpha \text{Tr}[H_1])^{-k} \text{Tr}[H_2] \]

\[ \times (-\text{Tr}[H_1])^{-m} \delta_{k+m} \left( \frac{3}{2} \right)^{N} \text{Tr}[H_1]^M \left( \frac{M + \frac{3}{2}}{M-m} \right)^{M-m} \]

\[ \times \left( (1 + \alpha \text{Tr}[H_1])^{-k} \text{Tr}[H_2] \right)^{k} \left( \frac{M!}{(M-k)!} \right)^{k} \left( \frac{\text{Tr}[H_1 H_2]}{\text{Tr}[H_1] \text{Tr}[H_2]} \right)^{k} \quad (A16) \]

Finally, after substituting Eq. (A16) into Eq. (A13), the structural integral for even power of \( r_{ij} \) is given by
$$R_e = \langle \phi_k | \phi_i \rangle \left( \binom{3}{2} \frac{1}{N} (\text{Tr}[H_1])^M \left[ \frac{M + \frac{3}{2}}{2} \right] (\text{Tr}[H_2])^N \right)$$

$$\times \sum_{k=0}^{\min(N,M)} \binom{N}{k} \frac{M!}{(M-k)!} \left( \frac{1}{k!} \frac{3}{2} \right)^k (\text{Tr}[H_1 H_2])^k (\text{Tr}[H_1]^M (\text{Tr}[H_2])^N)^k$$

(Eq. A17)

Expressions (A12) and (A17) will apply to $r_1$ and $r_2$, if we set $i = j$ and $i = 1, 2$.

For $N=1$, the structural integrals [Eqs. (A12) and (A17)] have the following simple form:

$$R_o = \langle \phi_k | \phi_i \rangle (\text{Tr}[H_2])^{1/2} \frac{1}{\Gamma} \left[ -\frac{1}{2} \frac{M - \frac{3}{2}}{2} \frac{\text{Tr}[H_1 H_2]}{\text{Tr}[H_1]^M (\text{Tr}[H_2])^N} \right]$$

$$R_e = \langle \phi_k | \phi_i \rangle \frac{1}{\Gamma} \left[ \frac{3}{2} \frac{\text{Tr}[H_1 H_2]}{\text{Tr}[H_2]^M (\text{Tr}[H_1]^M)^N} \right].$$

(A18)