Darwin and mass-velocity relativistic corrections in non-Born-Oppenheimer variational calculations

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The Pauli approach to account for the mass-velocity and Darwin relativistic corrections has been applied to the formalism for quantum mechanical molecular calculations that does not assume the Born-Oppenheimer (BO) approximation regarding separability of the electronic and nuclear motions in molecular systems. The corrections are determined using the first order perturbation theory and are derived for the non-BO wave function of a diatomic system expressed in terms of explicitly correlated Gaussian functions with premultipliers in the form of even powers of the internuclear distance. As a numerical example we used calculations of the transition energies for pure vibrational states of the HD^+ ion. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2236113]

I. INTRODUCTION

In order to achieve in quantum mechanical calculations of small molecular systems the accuracy matching that of high-resolution spectral measurements not only does one need to be able to accurately describe electronic correlations but also to account for nuclear motion and coupling between nuclear and electronic motions. Thus, it is very desirable to depart from the Born-Oppenheimer (BO) approximation regarding the separability of the electronic and nuclear motions. Moreover, one also needs to include relativistic corrections as their contribution to the total energy becomes quite noticeable when a comparison with accurate experimental data is made. In recent years we have been involved in developing an approach to perform quantum mechanical nonrelativistic molecular calculations without the BO approximation.[1–18] There have also been works of others in this area (see, for example, Refs. 19–21 and references therein). The central part of our approach has been the use of different forms of correlated Gaussian functions that are explicitly dependent on the distances between the particles (nuclei and electrons) forming the system under consideration. In particular, we used correlated Gaussians with premultipliers in the form of even powers of the distance between first and second particles (usually nuclei). We have demonstrated that with such functions one can achieve very high accuracy in ground- and excited-state calculations of diatomic systems with two or more electrons.[3–6,10,12–14,16–18] The high accuracy is facilitated by the variational optimization of the wave function that involves analytical first derivatives of the energy with respect to nonlinear parameters of the Gaussians.

In general, it is not possible to take the Dirac relativistic Hamiltonian and separate it into nonrelativistic and relativistic parts. The simplest and most traditional way to calculate the relativistic effect in atomic and molecular systems is based on the Pauli approximation. It provides a framework for describing a quantum particle with the accuracy of the order of α^2, where α is the fine structure constant. To get a more accurate description of a quantum system going beyond the Pauli approximation one can use the Breit-Pauli equation,[22] which explicitly includes operators describing the orbit-orbit and spin-orbit interactions, as well as other two-particle magnetic interactions. However, since the Breit-Pauli equation is not completely invariant with respect to the Lorentz transformation, an approximation is introduced in the calculation of the relativistic effects.

The Pauli approximation describes a state of a quantum particle represented by a two-component wave function, which is an eigenfunction of the nonrelativistic Hamiltonian. In such an approach the relativistic effects (and their corresponding operators) must be treated as perturbations and determined as the first order corrections to the nonrelativistic energy. This is a serious deficiency of the approach based on the Pauli approximation. This deficiency is the result of singularities that appear in the operators representing the rela-

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tivistic corrections. Extending the applicability of the Pauli approximation to systems with more than one particle can be achieved provided that in the Darwin contact term, all Coulombic interactions involving the particles in the system are included. Also the nonrelativistic wave function used in the calculations must give finite expectation values for all relativistic corrections involved in the Pauli approximation. In this work we have calculated relativistic corrections using the first order perturbation theory and the Pauli approximation. In the calculations we used the nonrelativistic wave functions expressed in terms of explicitly correlated Gaussian functions and obtained without assuming the Born-Oppenheimer approximation. Such wave functions can be generated for diatomic molecular systems with more that one (sigma) electron with the approach we have developed. It is important to mention that there were previous calculations concerning H_2^+ by Moss and Valenzano[23] where electronic relativistic corrections were determined using wave functions obtained in nonadiabatic calculations. However, the approach of Moss and Valenzano was restricted to one-electron diatomics and the possibility of its extension to systems with more electrons seems unlikely.

The need to perform highly accurate quantum mechanical calculations on small molecular systems is motivated by the progress in the high resolution gas-phase measurements of such molecular quantities as rovibrational and electronic excitation energies, electron affinities, ionization potentials, bond dissociation, and atomization energies that achieve the precision exceeding a tenth or even a hundredth of a wave number. This often presents a challenge to quantum mechanical studies of molecular systems because, in order to reach such an accuracy, not only nonrelativistic wave function must be computed with very high accuracy but also, even for small systems, the relativistic effects have to be taken into account.

As will be described later in this work, our non-BO approach is based on separating the center-of-mass motion of the system from the internal motion. The separation is achieved by transforming the laboratory Cartesian coordinate system to a new set of coordinates, the first three of which are the laboratory center-of-mass coordinates and the rest are internal Cartesian coordinates defined with respect to one of the nuclei (called the reference particle). Such a choice does not restrict the types of the molecular systems that can be calculated. Molecular systems with two and more nuclei can be considered in this framework.

The approach developed in this work for calculating the relativistic corrections to the non-BO energy within the Pauli approximation is applied to all vibrational states of the HD^+ ion with the zero total angular momentum. Such states are usually called "vibrational states," although if the Born-Oppenheimer approximation is not assumed, the vibrational motion is coupled with the electronic motion and the vibrational quantum number is not a good quantum number. H_2^+ and its isotopomers are the simplest model systems that show some interesting non-BO effects when excited to vibrational states near the dissociation threshold. As it had been known before and also shown in our recent non-BO calculations of average interparticle distances,[14,16] in the highest two vibrational levels of HD^+ and HT^+, the electron charge density is strongly polarized towards the deuteron and the systems can be described as a proton interacting with either a D atom in HD^+ or a T atom in HT^+. This very strong nonadiabatic effect differentiates the behavior of the H_2^+ ion, where in the highest vibrational states the electronic density is symmetrically distributed at the protons, from the asymmetric HD^+ and HT^+ ions. Due to these differences, it was interesting to see how the lack of the symmetry in the electronic charge distribution in HD^+ in the highest vibrational states affects the relativistic contributions to the energy, particularly those which are expected to be sensitive to such an effect.

II. THE METHOD USED IN THE CALCULATIONS

The total nonrelativistic Hamiltonian for a system with N particles (nuclei and electrons) in the laboratory Cartesian coordinate system has the following form:

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

with the masses, charges, and positions of the particles forming the system denoted as M_i, Q_i, and $\mathbf{R}_i$ ($\{\mathbf{R}\} = \{\mathbf{R}_1', \mathbf{R}_2', \ldots, \mathbf{R}_N'\}'$, where ($'$) denotes vector transposition), respectively (in a diatomic system the first two particles are the nuclei and the rest are electrons). The laboratory frame Hamiltonian includes the kinetic energy operator for each particle and Coulombic interactions between each pair of the particles. $R_{ij} = |\mathbf{R}_j - \mathbf{R}_i|$ are interparticle distances. In the first step we transform the Hamiltonian (1) by separating the center-of-mass motion, thereby reducing the N-particle problem to an $N-1=n$ pseudoparticle problem described by the internal Hamiltonian $\hat{H}$. In this transformation the laboratory Cartesian coordinate system is replaced by a system whose first three coordinates are the laboratory coordinates of the center of mass $\mathbf{r}_0$ and the remaining $3n$ coordinates are the Cartesian coordinates in the internal coordinate system whose origin is placed at the heaviest nucleus (particle 1 with mass M_1 called the reference particle). The other particles are referred to the reference particle using the Cartesian position vectors $\mathbf{r}_i$ defined as $\mathbf{r}_i = \mathbf{R}_{i+1} - \mathbf{R}_1$. The internal Hamiltonian $\hat{H}$ is

$$\hat{H} = -\frac{1}{2}\left(\sum_{i=1}^{n} \frac{1}{m_i} \nabla_{\mathbf{r}_i}^2 + \sum_{i=1}^{n} \sum_{i \neq j}^{n} \frac{1}{M_1} \nabla_{\mathbf{r}_i}' \nabla_{\mathbf{r}_j} \right) + V(\mathbf{r}), \tag{2}$$

where

$$V(\mathbf{r}) = \sum_{i=1}^{n} \frac{q_0 q_i}{r_i} + \sum_{j>i}^{n} \frac{q_i q_j}{r_{ij}}. \tag{3}$$

The separation of the internal Hamiltonian and the Hamiltonian of the motion of the center of mass is exact. The internal Hamiltonian (2) describes n pseudoparticles with charges $q_i = Q_{i+1}$ and reduced masses $m_i = M_1 M_{i+1}/(M_1 + M_{i+1})$ moving in the spherically symmetric potential of the charge of the reference particle. The motions of the pseudoparticles are coupled through the mass polarization term $\Sigma_{i \neq j}^{n} (1/M_1) \nabla_{\mathbf{r}_i}' \nabla_{\mathbf{r}_j}$ and through the Coulombic interac-

tions dependent on the distances of the pseudoparticles from the central charge, $r_i=|\mathbf{r}_i|$, and their relative distances, $r_{ij}=|\mathbf{R}_{j+1}-\mathbf{R}_{i+1}|=|\mathbf{r}_j-\mathbf{r}_i|$.

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

$$\hat{H}_{\mathrm{MV}}=-\frac{\alpha^2}{8}\sum_{i=1}^{N}\frac{1}{M_i^3}\nabla_{\mathbf{R}_i}^4, \tag{4}$$

$$\hat{H}_{\mathrm{D}}=\frac{\alpha^2}{8}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\frac{1}{M_i^2}\nabla_{\mathbf{R}_i}^2\frac{Q_iQ_j}{R_{ij}}. \tag{5}$$

Upon the transformation of the laboratory coordinate system to the internal system, the Darwin Hamiltonian (5) separates into a term dependent on the position vector of the center of mass in the laboratory frame, $\mathbf{r}_0$, and a term dependent on the internal coordinates, $\{\mathbf{r}\}=\{\mathbf{r}_1',\mathbf{r}_2',\ldots,\mathbf{r}_n'\}'$,

$$\hat{H}_{\mathrm{D}}(\mathbf{r},\mathbf{r}_0)=\hat{H}_{\mathrm{D}}(\mathbf{r}_0)+\hat{H}_{\mathrm{D}}(\mathbf{r}), \tag{6}$$

where

$$\hat{H}_{\mathrm{D}}(\mathbf{r}_0)=\frac{\alpha^2}{4}\frac{1}{m_0}\nabla_{\mathbf{r}_0}^2V(\mathbf{r})=0, \tag{7}$$

because $V(\mathbf{r})$ is independent of $\mathbf{r}_0$, and where

$$\hat{H}_{\mathrm{D}}(\mathbf{r})=\frac{\alpha^2}{8}\left[\sum_{i=1}^{n}\left(\frac{1}{M_1^2}+\frac{1}{M_{i+1}^2}\right)\nabla_{\mathbf{r}_i}^2\frac{q_0q_i}{r_i}+\sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{1}{M_{i+1}^2}\nabla_{\mathbf{r}_i}^2\frac{q_iq_j}{r_{ij}}\right]. \tag{8}$$

The Darwin correction can be calculated either directly using the operator (8), $\hat{H}_{\mathrm{D}}^{I}(\mathbf{r})=\hat{H}_{\mathrm{D}}(\mathbf{r})$ (we will call it here the first approach), or using an operator obtained from (8) by applying the Poisson equations (the second approach),

$$\nabla_{\mathbf{r}_i}^2\frac{1}{r_i}=-4\pi\delta(\mathbf{r}_i),\quad \nabla_{\mathbf{r}_i}^2\frac{1}{r_{ij}}=\nabla_{\mathbf{r}_j}^2\frac{1}{r_{ij}}=-4\pi\delta(\mathbf{r}_{ij}). \tag{9}$$

This results in the Darwin Hamiltonian in the following form:

$$\hat{H}_{\mathrm{D}}^{II}(\mathbf{r})=-\frac{\pi\alpha^2}{2}\left[\sum_{i=1}^{n}\left(\frac{1}{M_1^2}+\frac{1}{M_{i+1}^2}\right)q_0q_i\delta(\mathbf{r}_i)+\sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{1}{M_{i+1}^2}q_iq_j\delta(\mathbf{r}_{ij})\right]. \tag{10}$$

In the present work we used both Darwin Hamiltonians, $\hat{H}_{\mathrm{D}}^{I}(\mathbf{r})$ and $\hat{H}_{\mathrm{D}}^{II}(\mathbf{r})$, in the calculations. This was done to make sure that the algorithm for calculating the Darwin corrections was correctly implemented.

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

$$\hat{H}_{\mathrm{MV}}(\mathbf{r},\mathbf{r}_0)=\hat{H}_{\mathrm{MV}}(\mathbf{r}_0)+\hat{H}_{\mathrm{MV}}(\mathbf{r})+\hat{H}_{\mathrm{MV}}^{\mathrm{coupl}}(\mathbf{r}_0,\mathbf{r}), \tag{11}$$

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

$$\hat{H}_{\mathrm{MV}}(\mathbf{r})=-\frac{\alpha^2}{8}\left[\frac{1}{M_1^3}\left(\sum_{i=1}^{n}\nabla_{\mathbf{r}_i}\right)^4+\sum_{i=1}^{n}\frac{1}{M_{i+1}^3}\nabla_{\mathbf{r}_i}^4\right]. \tag{12}$$

The last term in Eq. (11), $\hat{H}_{\mathrm{MV}}^{\mathrm{coupl}}(\mathbf{r}_0,\mathbf{r})$, describes relativistic coupling between the motion of the center of mass and the internal motion. This effect is not considered in our calculations as we assume that the system as a whole is at rest, i.e., the center of mass is not moving.

The calculation of the relativistic correction to the energy of the internal motion of the system is performed for each state using the first order perturbation theory as the expectation value of the Hamiltonian representing the internal mass-velocity and Darwin contributions,

$$\hat{H}'(\mathbf{r})=\hat{H}_{\mathrm{MV}}(\mathbf{r})+\hat{H}_{\mathrm{D}}(\mathbf{r}). \tag{13}$$

In our works concerning non-BO calculations on small diatomic molecular systems[3–6,10,12–14,16–18] we used the explicitly correlated Gaussians (ECGs) involving functions with preexponential multipliers consisting of the internuclear distance $\mathbf{r}_1$ raised to a non negative even power m_k,

$$\phi_k=r_1^{m_k}\exp[-\mathbf{r}'(\mathbf{A}_k\otimes\mathbf{I}_3)\mathbf{r}]=r_1^{m_k}\exp[-\mathbf{r}'\bar{\mathbf{A}}_k\mathbf{r}], \tag{14}$$

where symbol $\bar{\mathbf{A}}_k$ denotes the Kronecker product $\bar{\mathbf{A}}_k=\mathbf{A}_k\otimes\mathbf{I}_3$, and $\mathbf{I}_3$ is 3×3 identity matrix. The above function is a one-center correlated Gaussian with exponential coefficients forming the symmetric matrix $\mathbf{A}_k$. $\mathbf{I}_3$ in Eq. (14) is the 3×3 identity matrix. ϕ_k are rotationally invariant functions as required by the symmetry of the internal ground-state problem described by the Hamiltonian (2). The presence of $r_1^{m_k}$ factor in (14) shifts the function peak away from the origin. This shift depends on the value of m_k and on the exponential parameters, $\mathbf{A}_k$. To describe a diatomic system, the maximum of the trial wave function in terms of r_1 should be around the equilibrium internuclear distance of the system. In a variational calculation the maxima of ϕ_k's are adjusted by optimization of m_k's and $\mathbf{A}_k$'s. More details on the Hamiltonian transformation and the selection of the basis functions for diatomic calculations the reader can obtain from our recent reviews.[1,2] The formulas for the matrix elements involving $\hat{H}_{\mathrm{MV}}(\mathbf{r})$, $\hat{H}_{\mathrm{D}}^{I}(\mathbf{r})$, and $\hat{H}_{\mathrm{D}}^{II}(\mathbf{r})$ operators and basis functions (14) are presented in the Appendixes.

In the present calculations we use the variational method, and the energy and the wave function for each state of HD^+ were obtained by minimizing the Rayleigh quotient,

$$E(\{c_k\},\{m_k\},\{\mathbf{A}_k\})=\min\frac{c'H(\{m_k\},\{\mathbf{A}_k\})c}{c'S(\{m_k\},\{\mathbf{A}_k\})c}, \tag{15}$$

with respect to the expansion coefficients of the wave function in terms of the basis functions c_k, the basis-function exponential parameters $\{\mathbf{A}_k\}$, and the preexponential powers $\{m_k\}$. The optimization is done separately for each state using an algorithm based on analytical derivatives of the energy,

TABLE I. Total non-BO energies ($E_{\text{non-BO}}$), mass-velocity and Darwin corrections, total energies that include relativistic corrections ($\Delta E_{\text{non-BO+rel}}$), and $v+1\rightarrow v$ transition energies that account ($\Delta E_{\text{non-BO}}$) and do not account ($\Delta E_{\text{non-BO+rel}}$) relativistic corrections. All energies are given in a.u., while transition energies are in cm^{-1}.

v	$E_{\text{non-BO}}$	Mass-velocity	Darwin	$E_{\text{non-BO+rel}}$	$\Delta E_{\text{non-BO}}$	$\Delta E_{\text{non-BO+rel}}$
0	−0.597 897 968 5	$-4.191\,71\times10^{-5}$	$3.464\,38\times10^{-5}$	−0.597 905 241 8	1912.9714	1913.0032
1	−0.589 181 829 4	$-4.097\,82\times10^{-5}$	$3.384\,97\times10^{-5}$	−0.589 188 958 0	1816.8394	1816.8684
2	−0.580 903 700 1	$-4.010\,31\times10^{-5}$	$3.310\,68\times10^{-5}$	−0.580 910 696 4	1723.5680	1723.5943
3	−0.573 050 546 3	$-3.928\,69\times10^{-5}$	$3.241\,03\times10^{-5}$	−0.573 057 422 9	1632.7829	1632.8068
4	−0.565 611 040 2	$-3.850\,76\times10^{-5}$	$3.174\,02\times10^{-5}$	−0.565 617 807 6	1544.1184	1544.1395
5	−0.558 575 519 3	$-3.781\,02\times10^{-5}$	3.11393×10^{-5}	−0.558 582 190 2	1457.2175	1457.2362
6	−0.551 935 948 0	$-3.717\,41\times10^{-5}$	3.05883×10^{-5}	−0.551 942 533 8	1371.7238	1371.7401
7	−0.545 685 914 4	$-3.659\,02\times10^{-5}$	$3.007\,84\times10^{-5}$	−0.545 692 426 2	1287.2790	1287.2933
8	−0.539 820 639 5	$-3.603\,23\times10^{-5}$	$2.958\,53\times10^{-5}$	−0.539 827 086 5	1203.5176	1203.5291
9	−0.534 337 009 7	$-3.552\,60\times10^{-5}$	$2.913\,11\times10^{-5}$	−0.534 343 404 6	1120.0621	1120.0720
10	−0.529 233 631 2	$-3.507\,30\times10^{-5}$	$2.872\,29\times10^{-5}$	−0.529 239 981 2	1036.5185	1036.5253
11	−0.524 510 905 3	$-3.468\,16\times10^{-5}$	$2.836\,26\times10^{-5}$	−0.524 517 224 3	952.4686	952.4735
12	−0.520 171 139 2	$-3.430\,58\times10^{-5}$	$2.800\,92\times10^{-5}$	−0.520 177 435 8	867.4591	867.4614
13	−0.516 218 704 7	$-3.400\,66\times10^{-5}$	2.77205×10^{-5}	−0.516 224 990 8	781.0053	781.0056
14	−0.512 660 182 8	$-3.372\,80\times10^{-5}$	$2.744\,32\times10^{-5}$	−0.512 666 467 5	692.5615	692.5594
15	−0.509 504 640 3	$-3.349\,54\times10^{-5}$	2.72009×10^{-5}	−0.509 510 934 8	601.5306	601.5257
16	−0.506 763 865 3	$-3.331\,05\times10^{-5}$	2.69939×10^{-5}	−0.506 770 181 9	507.2464	507.2391
17	−0.504 452 680 7	$-3.316\,57\times10^{-5}$	$2.681\,57\times10^{-5}$	−0.504 459 030 7	408.9828	408.9717
18	−0.502 589 218 0	$-3.308\,81\times10^{-5}$	2.66878×10^{-5}	−0.502 595 618 3	306.0416	306.0291
19	−0.501 194 790 1	$-3.307\,44\times10^{-5}$	2.66175×10^{-5}	−0.501 201 247 0	198.0420	198.0261
20	−0.500 292 444 4	$-3.309\,48\times10^{-5}$	2.65655×10^{-5}	−0.500 298 9737	83.8591	83.8393
21	−0.499 910 354 2	$-3.319\,63\times10^{-5}$	2.65765×10^{-5}	−0.499 916 973 9	9.7834	9.7791
22	−0.499 865 777 6	$-3.323\,65\times10^{-5}$	$2.659\,69\times10^{-5}$	−0.499 872 417 1	0.4307	
D atom	−0.499 863 815 2					

$E(\{c_k\},\{m_k\},\{\mathbf{A}_k\})$, with respect to elements of $\mathbf{A}_k$.

In general, simultaneous optimization of the energy functional (15) with respect to nonlinear parameters of all basis functions represents a difficult and very time consuming computational task when the number of basis functions exceeds a few hundreds. To achieve the best results in the parameter optimization with the least computational effort, we have implemented a hybrid method that combines the gradient based optimization with the stochastic selection method.[12,13] The strategy is based on alternating the gradient based and the stochastic based optimizations in growing the basis set from a relatively small initial set to a much larger final set. The small initial basis set is obtained by means of simultaneous optimization of all nonlinear parameters. The basis set for each vibrational state was generated in a separate calculation. To achieve high accuracy we used 2500 basis functions for all states, except $v=23$ state, where the number of basis functions was 4000. The range of the preexponential powers $\{m_k\}$ used was 0–250, and all the powers were partially optimized for each state.

For all 23 ($v=0,\ldots,22$) vibrational states of HD^+ we calculated the expectation values of the relativistic Hamiltonian (11) and added it to the variational energy of that state. Those values were used to calculate the transition energies. The nuclear masses used in the calculations were $m_p=1836.152\,672\,61m_e$ and $m_d=3670.482\,965\,2m_e$, which were taken from Ref. 25. Here, m_e stands for the mass of the electron. The value of the fine structure constant was $\alpha=1/137.035\,999\,11$.

III. THE RESULTS AND DISCUSSION

The transition energies for all 23 rotationless bound vibrational states of HD^+ are presented in Table I. Both nonrelativistic non-BO energies and energies including the relativistic corrections are shown. In the table we also include the values of individual Darwin and mass-velocity corrections. The Darwin corrections were calculated using both $\hat{H}_{\text{D}}^{I}$ and $\hat{H}_{\text{D}}^{II}$ and the results agreed within the numerical accuracy. The relativistic electronic corrections for HD^+ were calculated before by Howells and Kennedy[26] using the first order perturbation theory and the BO wave functions obtained for a wide range of interunclear distances. These results were then averaged over vibrational wave functions obtained by solving the vibrational equations with the potential energy taken from the BO calculations. The comparison of our total relativistic correction for each vibrational state (i.e., the sum of the Darwin and mass-velocity corrections) with that obtained by Howells and Kennedy[26] is shown in Table II. As one can notice, the results are not identical, but close. In general our corrections are 0.005 cm^{-1} lower in magnitude than the corrections of Howells and Kennedy. The differences may be caused by several factors such as the use of the reduced electron mass in our calculations versus the use of the real electron mass in their calculations, not assuming the BO approximation in our approach versus assuming this approach in theirs, the differences in the basis functions and in their abilities to describe the contact densities, etc. It is interesting to mention here a comparison of the relativistic corrections calculated for H_2^+ by Howells and Kennedy in the

TABLE II. Comparison of the relativistic corrections (sum of MV and Darwin) obtained in this work with those of Howells and Kennedy.(Ref. 26). All quantities are in cm^{-1}.

v	This work	Ref. 26
0	−1.5963	−1.6015
1	−1.5645	−1.5696
2	−1.5355	−1.5405
3	−1.5092	−1.5141
4	−1.4853	−1.4904
5	−1.4641	−1.4691
6	−1.4454	−1.4503
7	−1.4292	−1.4340
8	−1.4150	−1.4199
9	−1.4035	−1.4081
10	−1.3937	−1.3986
11	−1.3869	−1.3915
12	−1.3820	−1.3867
13	−1.3796	−1.3842
14	−1.3793	−1.3841
15	−1.3815	−1.3864
16	−1.3863	−1.3913
17	−1.3937	−1.3989
18	−1.4047	−1.4091
19	−1.4171	−1.4221
20	−1.4330	−1.4377
21	−1.4529	−1.4564
22	−1.4572	−1.4605

same work where they presented the HD^+ results with the results obtained by Moss and Valenzano[23] and shown in the latter paper. This comparison shows similar differences between the relativistic corrections for the H_2^+ vibrational energies obtained by the two teams to the differences between our corrections and those obtained by Moss and Valenzano for HD^+. This seems to indicate that in calculating relativistic corrections it is difficult to achieve higher accuracy than about 0.005 cm^{-1} due to the nature of the operators involved in the calculations (i.e., higher derivatives and Dirac delta functions).

The non-BO energies without the relativistic corrections shown in Table I are virtually identical to those presented before in Ref. 14. The transition energies corrected for the relativistic effects in the lower part of the spectrum are lower by 0.01–0.03 cm^{-1} than their uncorrected counterparts. This trend reverses in the upper part where the transition energies obtained from the energies corrected for the relativistic effects are lower than those obtained from uncorrected energies. Although in general the relativistic corrections to the transition energies are small, they are not negligible and, for most transitions, they are a little larger than the usual precision of the experiment. Thus, their inclusion should result in improved accuracy of the predicted transition energies as was the case for the transition energies we recently calculated for the HeH^+ (Ref. 24) ion where a direct comparison with the experimentally determined three lowest vibrational transitions was possible.

There is one additional observation one can make upon comparing the relativistically corrected transition energies with the uncorrected ones. It concerns the highest transition in the spectrum between the $v=22$ and $v=21$ levels whose relativistically uncorrected transition energy is 9.7790 cm^{-1} and the corrected one is 9.7743 cm^{-1}. As we determined in our previous work,[14] in both $v=21$ and $v=22$ states, HD^+ can be described as a D atom interacting with a distant proton. This is different than in the lower states, where the degree of the electron charge polarization is much lower. The $22 \rightarrow 21$ transition is somewhat an anomaly as far as the relativistic corrections are concerned. Based on the transitions just below the $22 \rightarrow 21$ transition one would expect to see an over 0.02 cm^{-1} decrease of the transition energies when the relativistic effects are included. However, the relativistically corrected and uncorrected transition energies are almost identical. We attribute this lack of change to the unusually high electronic polarization of HD^+ in the $v=21$ and $v=22$ states.

IV. SUMMARY

In this work we described the algorithms for calculating mass-velocity and Darwin relativistic corrections to the non-Born-Oppenheimer energy of diatomic systems with σ electrons. With this, for the first time a general framework for calculating these two relativistic effects for systems with more than one electron was presented and implemented within an approach that does not separate the electronic and nuclear motions (as it happens when the BO approximation is assumed). Thus in the calculation we can describe on an equal footing the relativistic effects due to electrons and nuclei, as well as effects due to interactions between these two types of particles. The derivations of the integrals involving explicitly correlated Gaussian functions for both the Darwin and mass-velocity corrections are lengthy but lead to expressions that can be readily programed. The code for the corrections has been integrated into our non-BO diatomic computer program that has been efficiently parallelized using message passing interface (MPI).

As we have demonstrated in the non-BO calculations for some diatomic systems [see, for example, the recently presented calculations for HeH^+ (Ref. 24)], our approach is capable of producing total and transition energies with accuracy that matches that of high resolution experiments. In our pursuit to develop a predictive method for calculating diatomic rovibrational spectra with the accuracy of the state-of-the-art high resolution experiment, we have to account for the relativistic effects. Including the Darwin and mass-velocity effects is the start. Next stage will be the inclusion of magnetic spin-spin, spin-orbit, and orbit-orbit interactions. It is definitely an exciting task to push the theoretical development to its limits as described by the nonrelativistic and relativistic quantum mechanics.

Finally, we hope that the relativistically corrected transition energies determined in this work will be helpful in assisting the experiment. We need to add that at present time the non-BO calculations such as those for HD^+ (and to a much higher degree for systems with more electrons) require a lot of computational time. We hope that the progress in the computer hardware will enable calculations of spectra of sys-

tems with three and four electrons with a similar accuracy as it is currently possible for diatomic systems with one or two electrons.

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APPENDIX A: SOME AUXILIARY FORMULAS

Two types of functions are used in the derivations,

- $f_k = \exp(-\mathbf{r}'\bar{\mathbf{A}}_k\mathbf{r})$,
- $\phi_k = r_1^{m_k}\exp(-\mathbf{r}'\bar{\mathbf{A}}_k\mathbf{r}) = (\mathbf{r}'\bar{\mathbf{J}}_{11}\mathbf{r})^{m_k/2}\exp(-\mathbf{r}'\bar{\mathbf{A}}_k\mathbf{r})$,

where the matrix $\bar{\mathbf{J}}_{11}=\mathbf{J}_{11}\otimes\mathbf{I}_3$ is a partial case of matrix $\bar{\mathbf{J}}_{ij}$, which we will define in the following way:

$$(\mathbf{J}_{ij})_{\alpha\beta} = \delta_{\alpha i}\delta_{i\beta} + \delta_{\alpha j}\delta_{j\beta} - \delta_{\alpha j}\delta_{i\beta} - \delta_{\alpha i}\delta_{j\beta}, \quad i \neq j,$$

$$(\mathbf{J}_{ii})_{\alpha\beta} = \delta_{\alpha i}\delta_{i\beta}, \tag{A1}$$

and where $\delta_{\alpha\beta}$ is the Kronecker symbol. By setting $m_k=0$ one gets the f_k functions from the ϕ_k functions. In order to simplify the notations we will be denoting the sum of the powers of ϕ_k and ϕ_l as $p \equiv (m_k+m_l)/2 \equiv m_{kl}/2$.

For matrices $\bar{\mathbf{B}}=\mathbf{B}\otimes\mathbf{I}_3$ and $\mathbf{B}$ we will use the following relations:

$$\mathrm{tr}[\bar{\mathbf{B}}] = 3\,\mathrm{tr}[\mathbf{B}],$$

$$|\bar{\mathbf{B}}| = |\mathbf{B}|^3.$$

Here and below vertical bars around a matrix denote the determinant of the matrix, while $\mathrm{tr}[\cdots]$ stands for the trace of a matrix.

To avoid any confusion, we will not assume that the matrices appearing in the integrals below are symmetric unless explicitly stated.

The first and second differentials of the ϕ_k function have the following forms:

$$\partial_\alpha\phi_k = \phi_k[m_k r_1^{-2}(\bar{\mathbf{J}}_{11}\mathbf{r})_\alpha - 2(\bar{\mathbf{A}}_k\mathbf{r})_\alpha] \tag{A2}$$

and

$$\begin{aligned}\partial_\alpha\partial_\beta\phi_k = \phi_k[&m_k(m_k-2)r_1^{-4}(\mathbf{r}'\bar{\mathbf{J}}_{11})_\alpha(\bar{\mathbf{J}}_{11}\mathbf{r})_\beta \\ &- 2m_k r_1^{-2}((\mathbf{r}'\bar{\mathbf{J}}_{11})_\alpha(\bar{\mathbf{A}}_k\mathbf{r})_\beta + (\mathbf{r}'\bar{\mathbf{A}}_k)_\alpha(\bar{\mathbf{J}}_{11}\mathbf{r})_\beta) \\ &+ 4(\mathbf{r}'\bar{\mathbf{A}}_k)_\alpha(\bar{\mathbf{A}}_k\mathbf{r})_\beta + m_k r_1^{-2}(\bar{\mathbf{J}}_{11})_{\beta\alpha} - 2(\bar{\mathbf{A}}_k)_{\beta\alpha}].\end{aligned} \tag{A3}$$

It follows from here that

$$\bar{\mathbf{B}}^{\alpha\beta}\partial_\beta\phi_k = \phi_k[m_k r_1^{-2}(\bar{\mathbf{B}}\bar{\mathbf{J}}_{11}r)^\alpha - 2(\bar{\mathbf{B}}\bar{\mathbf{A}}_k\mathbf{r})^\alpha], \tag{A4}$$

$$\begin{aligned}\nabla'_{\mathbf{r}}\bar{\mathbf{B}}\nabla_{\mathbf{r}} = \partial_\alpha(\bar{\mathbf{B}})^{\alpha\beta}\partial_\beta\phi_k = \phi_k[&m_k(m_k+1)r_1^{-2}\mathbf{B}_{11} \\ &- 2m_k r_1^{-2}\mathbf{r}'(\bar{\mathbf{J}}_{11}\bar{\mathbf{B}}\bar{\mathbf{A}}_k + \bar{\mathbf{A}}_k\bar{\mathbf{B}}\bar{\mathbf{J}}_{11})\mathbf{r} \\ &+ 4\mathbf{r}'\bar{\mathbf{A}}_k\bar{\mathbf{B}}\bar{\mathbf{A}}_k\mathbf{r} - 6\,\mathrm{tr}(\mathbf{A}_k\mathbf{B})].\end{aligned} \tag{A5}$$

Throughout our derivations we will extensively use the relation

$$\int_{-\infty}^{\infty}\exp[-\mathbf{r}'\bar{\mathbf{A}}\mathbf{r}]d\mathbf{r} = \pi^{3n/2}|\bar{\mathbf{A}}|^{-1/2}, \tag{A6}$$

which holds for positive definite symmetric matrix $\mathbf{A}$. According to (A6) the overlap of f_k and f_l is

$$\langle f_k|f_l\rangle = \pi^{3n/2}|\mathbf{A}|^{-3/2}. \tag{A7}$$

Expressing r_1^{2p} and r_{ij}^{-1} in the following way:

$$r_1^{2p} = (-)^p \left.\frac{\partial^p \exp[-u\mathbf{r}'\bar{\mathbf{J}}_{11}\mathbf{r}]}{\partial u^p}\right|_{u=0} \tag{A8}$$

and

$$\frac{1}{r_{ij}} = \frac{2}{\sqrt{\pi}}\int_0^\infty \exp[-t^2\mathbf{r}'\bar{\mathbf{J}}_{ij}\mathbf{r}]dt, \tag{A9}$$

and using (A6) we can evaluate the following useful integral $(2p=m_{kl}-q)$:

$$\begin{aligned}\left\langle \phi_k\left|r_1^{-q}\frac{1}{r_{ij}}\right|\phi_l\right\rangle &= \left\langle f_k\left|r_1^{2p}\frac{1}{r_{ij}}\right|f_l\right\rangle \\ &= \frac{2}{\sqrt{\pi}}(-)^p\frac{\partial^p}{\partial u^p}\int_0^\infty\int_{-\infty}^\infty \exp[-\mathbf{r}'(\bar{\mathbf{A}}_{kl}+u\bar{\mathbf{J}}_{11} \\ &\quad + t^2\bar{\mathbf{J}}_{ij})\mathbf{r}]\,d\mathbf{r}dt|_{u=0}.\end{aligned} \tag{A10}$$

We can differentiate (A7) with respect to $(\bar{\mathbf{A}}_{kl})_{\alpha\beta}$,

$$\frac{\partial\langle f_k|f_l\rangle}{\partial(\bar{\mathbf{A}}_{kl})_{\alpha\beta}} = \int_{-\infty}^{\infty}\frac{\partial f_k f_l}{\partial(\bar{\mathbf{A}}_{kl})_{\alpha\beta}}d\mathbf{r}, \tag{A11}$$

which yields

$$\langle f_k|\mathbf{r}_\alpha\mathbf{r}_\beta|f_l\rangle = -\frac{\partial\langle f_k|f_l\rangle}{\partial(\bar{\mathbf{A}}_{kl})_{\alpha\beta}}. \tag{A12}$$

This result can be generalized as

$$\langle\phi_k|g(\mathbf{r})\mathbf{r}_\alpha\mathbf{r}_\beta|\phi_l\rangle = -\frac{\partial\langle\phi_k|g(\mathbf{r})|\phi_l\rangle}{\partial(\bar{\mathbf{A}}_{kl})_{\alpha\beta}}, \tag{A13}$$

$$\langle\phi_k|g(\mathbf{r})\mathbf{r}_\alpha\mathbf{r}_\beta\mathbf{r}_\rho\mathbf{r}_\gamma|\phi_l\rangle = \frac{\partial^2\langle\phi_k|g(\mathbf{r})|\phi_l\rangle}{\partial(\bar{\mathbf{A}}_{kl})_{\alpha\beta}\partial(\bar{\mathbf{A}}_{kl})_{\rho\gamma}}, \tag{A14}$$

where $g(\mathbf{r})$ is an arbitrary function of $\mathbf{r}$ that does not depend on $(\bar{\mathbf{A}}_{kl})_{\alpha\beta}$, for example, r_1^{-n} or $1/r_{ij}$.

Calculation of determinants can be handled using the following theorem.

Theorem (on the inverse matrix and the determinant[27]). If

- $\mathbf{G}$ and $\mathbf{G}+\mathbf{H}$ are nonsingular matrices,

- rank $(\mathbf{H})=r>0$,
- $\mathbf{H}=\mathbf{H}_1+\mathbf{H}_2+\cdots+\mathbf{H}_r$, where rank $(\mathbf{H}_k)=1$, $1\leqslant k\leqslant r$, and
- $\mathbf{C}_{k+1}=\mathbf{G}+\mathbf{H}_1+\cdots+\mathbf{H}_k$ is nonsingular for $k=1,\ldots,r$ $(\mathbf{C}_1=\mathbf{G})$.

then,

(1) $\mathbf{C}_{k+1}^{-1}=\mathbf{C}_k^{-1}-v_k\mathbf{C}_k^{-1}\mathbf{H}_k\mathbf{C}_k^{-1}$, where $v_k^{-1}=1+\mathrm{tr}\,\mathbf{C}_k^{-1}\mathbf{H}$, $1\leqslant k\leqslant r$.

(2) $|\mathbf{G}+\mathbf{H}|=(v_1v_2,\ldots,v_r)^{-1}|\mathbf{G}|$.

Using the above theorem we can express determinants $|\mathbf{I}_n+a\mathbf{H}_1|$ and $|\mathbf{I}_n+a\mathbf{H}_1+b\mathbf{H}_2|$ as a sum. To do this we will set

$$\mathbf{C}_1^{-1}=\mathbf{I}_n,$$

$$v_1^{-1}=1+a\ \mathrm{tr}\,\mathbf{H}_1,$$

$$\mathbf{C}_2^{-1}=(1+a\ \mathrm{tr}\,\mathbf{H}_1)^{-1}\mathbf{H}_1,$$

$$v_2^{-1}=1+b\ \mathrm{tr}\,\mathbf{H}_2-(1+a\ \mathrm{tr}\,\mathbf{H}_1)^{-1}ab\ \mathrm{tr}(\mathbf{H}_1\mathbf{H}_2).$$

The results are

$$|\mathbf{I}_n+a\mathbf{H}_1|=1+a\ \mathrm{tr}\,\mathbf{H}_1 \tag{A15}$$

and

$$|\mathbf{I}_n+a\mathbf{H}_1+b\mathbf{H}_2|=1+a\ \mathrm{tr}\,\mathbf{H}_1+b\ \mathrm{tr}\,\mathbf{H}_2+a\,b(\mathrm{tr}\,\mathbf{H}_1\ \mathrm{tr}\,\mathbf{H}_2-\mathrm{tr}(\mathbf{H}_1\mathbf{H}_2)). \tag{A16}$$

We will also be using the Leibniz formula for the derivative of a product of two functions f and g,

$$\frac{\partial^q}{\partial x^q}f(x)g(x)=\sum_{s=0}^{q}\frac{\Gamma[q+1]}{\Gamma[s+1]\Gamma[q-s+1]}f^{(q-s)}g^{(s)}. \tag{A17}$$

APPENDIX B: MASS-VELOCITY (MV) TERM

After the transformation from the laboratory coordinate system to the internal coordinate system the MV Hamiltonian has the following form (n is the number of pseudoparticles, in the case of HD^+ $n=2$):

$$\hat{H}_{\mathrm{MV}}(\mathbf{r})=-\frac{\alpha^2}{8}\left[\frac{1}{M_1^3}\left(\sum_{i=1}^{n}\nabla_{\mathbf{r}_i}\right)^4+\sum_{i=1}^{n}\frac{1}{M_{i+1}^3}\nabla_{\mathbf{r}_i}^4\right]. \tag{B1}$$

The matrix elements that need to be calculated are

$$\langle\phi_k|\hat{H}_{\mathrm{MV}}|\phi_l\rangle=-\frac{\alpha^2}{8}\left(\frac{1}{M_1^3}\langle\nabla_{\mathbf{r}}'\bar{\mathbf{J}}\nabla_{\mathbf{r}}\phi_k|\nabla_{\mathbf{r}}'\bar{\mathbf{J}}\nabla_{\mathbf{r}}\phi_l\rangle+\sum_{i=1}^{n}\frac{1}{M_{i+1}^3}\langle\nabla_{\mathbf{r}}'\bar{\mathbf{J}}_{ii}\nabla_{\mathbf{r}}\phi_k|\nabla_{\mathbf{r}}'\bar{\mathbf{J}}_{ii}\nabla_{\mathbf{r}}\phi_l\rangle\right), \tag{B2}$$

where we used the matrix $\mathbf{J}$ (with no indices), whose elements are equal to one: $\mathbf{J}_{\alpha\beta}=1$. Matrix $\mathbf{J}_{ii}$ is defined in (A1).

Only one type of integral appears in the expression for the $\hat{H}_{\mathrm{MV}}$ matrix elements: $\langle\nabla_{\mathbf{r}}'\bar{\mathbf{D}}\nabla_{\mathbf{r}}\phi_k|\nabla_{\mathbf{r}}'\bar{\mathbf{D}}\nabla_{\mathbf{r}}\phi_l\rangle$, where $\bar{\mathbf{D}}$ is either $\bar{\mathbf{J}}$ or $\bar{\mathbf{J}}_{ii}$. To compute it we can express it through the following elementary integrals:

$$\begin{aligned}\langle\nabla_{\mathbf{r}}'\bar{\mathbf{D}}\nabla_{\mathbf{r}}\phi_k|\nabla_{\mathbf{r}}'\bar{\mathbf{D}}\nabla_{\mathbf{r}}\phi_l\rangle&=36\ \mathrm{tr}[\mathbf{A}_k\mathbf{D}]\mathrm{tr}[\mathbf{A}_l\mathbf{D}]\times\langle\phi_k|\phi_l\rangle-24\ \mathrm{tr}[\mathbf{A}_k\mathbf{D}]\times\langle\phi_k|\mathbf{r}'\bar{\mathbf{A}}_l\bar{\mathbf{D}}\bar{\mathbf{A}}_l\mathbf{r}|\phi_l\rangle-24\ \mathrm{tr}[\mathbf{A}_l\mathbf{D}]\times\langle\phi_k|\mathbf{r}'\bar{\mathbf{A}}_k\bar{\mathbf{D}}\bar{\mathbf{A}}_k\mathbf{r}|\phi_l\rangle\\&+16\times\langle\phi_k|\mathbf{r}'\bar{\mathbf{A}}_k\bar{\mathbf{D}}\bar{\mathbf{A}}_k\mathbf{r}\mathbf{r}'\bar{\mathbf{A}}_l\bar{\mathbf{D}}\bar{\mathbf{A}}_l\mathbf{r}|\phi_l\rangle-6m_k(m_k+1)\mathrm{tr}[\mathbf{A}_l\mathbf{D}]\mathbf{D}_{11}\times\langle\phi_k|r_1^{-2}|\phi_l\rangle-6m_l(m_l\\&+1)\mathrm{tr}[\mathbf{A}_k\mathbf{D}]\mathbf{D}_{11}\times\langle\phi_k|r_1^{-2}|\phi_l\rangle+4m_k(m_k+1)\mathbf{D}_{11}\times\langle\phi_k|r_1^{-2}\mathbf{r}'\bar{\mathbf{A}}_l\bar{\mathbf{D}}\bar{\mathbf{A}}_l\mathbf{r}|\phi_l\rangle+4m_l(m_l+1)\mathbf{D}_{11}\\&\times\langle\phi_k|r_1^{-2}\mathbf{r}'\bar{\mathbf{A}}_k\bar{\mathbf{D}}\bar{\mathbf{A}}_k\mathbf{r}|\phi_l\rangle+12m_k\ \mathrm{tr}(\mathbf{A}_l\mathbf{D})\times\langle\phi_k|r_1^{-2}\mathbf{r}'(\bar{\mathbf{A}}_k\bar{\mathbf{D}}\bar{\mathbf{J}}_{11}+\bar{\mathbf{J}}_{11}\bar{\mathbf{D}}\bar{\mathbf{A}}_k)\mathbf{r}|\phi_l\rangle+12m_l\ \mathrm{tr}(\mathbf{A}_k\mathbf{D})\\&\times\langle\phi_k|r_1^{-2}\mathbf{r}'(\bar{\mathbf{A}}_l\bar{\mathbf{D}}\bar{\mathbf{J}}_{11}+\bar{\mathbf{J}}_{11}\bar{\mathbf{D}}\bar{\mathbf{A}}_l)\mathbf{r}|\phi_l\rangle-8m_k\times\langle\phi_k|r_1^{-2}\mathbf{r}'(\bar{\mathbf{A}}_k\bar{\mathbf{D}}\bar{\mathbf{J}}_{11}+\bar{\mathbf{J}}_{11}\bar{\mathbf{D}}\bar{\mathbf{A}}_k)\mathbf{r}\mathbf{r}'\bar{\mathbf{A}}_l\bar{\mathbf{D}}\bar{\mathbf{A}}_l\mathbf{r}|\phi_l\rangle-8m_l\\&\times\langle\phi_k|r_1^{-2}\mathbf{r}'(\bar{\mathbf{A}}_l\bar{\mathbf{D}}\bar{\mathbf{J}}_{11}+\bar{\mathbf{J}}_{11}\bar{\mathbf{D}}\bar{\mathbf{A}}_l)\mathbf{r}\mathbf{r}'\bar{\mathbf{A}}_k\bar{\mathbf{D}}\bar{\mathbf{A}}_k\mathbf{r}|\phi_l\rangle+m_k(m_k+1)m_l(m_l+1)(\mathbf{D}_{11})^2\times\langle\phi_k|r_1^{-4}|\phi_l\rangle\\&-2m_k(m_k+1)m_l\mathbf{D}_{11}\times\langle\phi_k|r_1^{-4}\mathbf{r}'(\bar{\mathbf{A}}_l\bar{\mathbf{D}}\bar{\mathbf{J}}_{11}+\bar{\mathbf{J}}_{11}\bar{\mathbf{D}}\bar{\mathbf{A}}_l)\mathbf{r}|\phi_l\rangle-2m_km_l(m_l+1)\mathbf{D}_{11}\times\langle\phi_k|r_1^{-4}\mathbf{r}'(\bar{\mathbf{A}}_k\bar{\mathbf{D}}\bar{\mathbf{J}}_{11}\\&+\bar{\mathbf{J}}_{11}\bar{\mathbf{D}}\bar{\mathbf{A}}_k)\mathbf{r}|\phi_l\rangle+4m_km_l\times\langle\phi_k|r_1^{-4}\mathbf{r}'(\bar{\mathbf{A}}_k\bar{\mathbf{D}}\bar{\mathbf{J}}_{11}+\bar{\mathbf{J}}_{11}\bar{\mathbf{D}}\bar{\mathbf{A}}_k)\mathbf{r}\mathbf{r}'(\bar{\mathbf{A}}_l\bar{\mathbf{D}}\bar{\mathbf{J}}_{11}+\bar{\mathbf{J}}_{11}\bar{\mathbf{D}}\bar{\mathbf{A}}_l)\mathbf{r}|\phi_l\rangle.\end{aligned}$$

Thus, to carry out the calculations of the MV correction one needs the following integrals: $\langle\phi_k|r_1^{-q}|\phi_l\rangle$, $\langle\phi_k|r_1^{-q}\mathbf{r}'\bar{\mathbf{B}}\mathbf{r}|\phi_l\rangle$, and $\langle\phi_k|r_1^{-q}\mathbf{r}'\bar{\mathbf{B}}\mathbf{r}\mathbf{r}'\bar{\mathbf{C}}\mathbf{r}|\phi_l\rangle$, where $q=0$, 2, and 4. We present the expressions for those integrals below.

1. Integral $\langle\phi_k|r_1^{-q}|\phi_l\rangle$

We start with the integral $\langle\phi_k|r_1^{-q}|\phi_l\rangle$. According to (A10) one can write

$$\langle\phi_k|r_1^{-q}|\phi_l\rangle = (-1)^p \frac{\partial^p}{\partial a^p}\int_{-\infty}^{\infty} \exp\left[-\mathbf{r}'(\bar{\mathbf{A}}_{kl}+a\bar{\mathbf{J}}_{11})\mathbf{r}\right]d\mathbf{r}|_{a=0}(-1)^p|\mathbf{A}_{kl}|^{-3/2}\pi^{3n/2}\frac{\partial^p}{\partial a^p}\,|\mathbf{I}_n + a\mathbf{J}_{11}\mathbf{A}_{kl}^{-1}|^{-3/2}|_{a=0}$$

$$= (-1)^p|\mathbf{A}_{kl}|^{-3/2}\pi^{3n/2}\frac{\partial^p}{\partial a^p}\,(1+a\,\mathrm{tr}[\mathbf{J}_{11}\mathbf{A}_{kl}^{-1}]^{-3/2}\,|_{a=0} = (-1)^p\langle f_k|f_l\rangle(-)^p\frac{2}{\sqrt{\pi}}\Gamma[p+3/2](\mathbf{A}_{kl}^{-1})_{11}^p$$

$$= \frac{2}{\sqrt{\pi}}\langle f_k|f_l\rangle\Gamma[(m_{kl}-q)/2+3/2](\mathbf{A}_{kl}^{-1})_{11}^{(m_{kl}-q)/2}, \tag{B3}$$

where (A6), (A8), and (A15) were used. After simplification we obtain

$$\langle\phi_k|r_1^{-q}|\phi_l\rangle = \frac{2}{\sqrt{\pi}}\langle f_k|f_l\rangle\Gamma[(m_{kl}-q)/2+3/2](\mathbf{A}_{kl}^{-1})_{11}^{(m_{kl}-q)/2}. \tag{B4}$$

In the case of $q=0$, 2, and 4 the corresponding expressions are

$$\langle\phi_k|\phi_l\rangle = \frac{2}{\sqrt{\pi}}\langle f_k|f_l\rangle\Gamma[m_{kl}+3/2](\mathbf{A}_{kl}^{-1})_{11}^{m_{kl}/2}, \tag{B5}$$

$$\langle\phi_k|r_1^{-2}|\phi_l\rangle = 2(m_{kl}+1)^{-1}(\mathbf{A}_{kl}^{-1})_{11}^{-1}\langle\phi_k|\phi_l\rangle, \tag{B6}$$

$$\langle\phi_k|r_1^{-4}|\phi_l\rangle = 4(m_{kl}^2-1)^{-1}(\mathbf{A}_{kl}^{-1})_{11}^{-2}\langle\phi_k|\phi_l\rangle. \tag{B7}$$

2. Integral $\langle\phi_k|r_1^{-q}\mathbf{r}'\bar{\mathbf{B}}\mathbf{r}|\phi_l\rangle$

This integral is evaluated using the following relation:

$$\langle\phi_k|r_1^{-q}\mathbf{r}'\bar{\mathbf{B}}\mathbf{r}|\phi_l\rangle = \langle\phi_k|r_1^{-q}\mathbf{r}_\alpha\mathbf{r}_\beta|\phi_l\rangle\bar{\mathbf{B}}^{\alpha\beta}. \tag{B8}$$

Together with (A13) we have

$$\langle\phi_k|r_1^{-q}\mathbf{r}_\alpha\mathbf{r}_\beta|\phi_l\rangle = -\frac{\partial\langle\phi_k|r_1^{-q}|\phi_l\rangle}{\partial(\bar{\mathbf{A}}_{kl})_{\alpha\beta}}. \tag{B9}$$

To determine the above derivative the following identities are used (for details see Ref. 28):

$$\frac{\partial(\bar{\mathbf{A}}_{kl}^{-1})_{\rho\gamma}}{\partial(\bar{\mathbf{A}}_{kl})_{\alpha\beta}} = -(\bar{\mathbf{A}}_{kl}^{-1})_{\rho\alpha}(\bar{\mathbf{A}}_{kl}^{-1})_{\beta\gamma} \tag{B10}$$

and

$$\frac{\partial\,\mathrm{tr}(\bar{\mathbf{J}}_{11}\bar{\mathbf{A}}_{kl}^{-1})}{\partial(\bar{\mathbf{A}}_{kl})_{\alpha\beta}} = -(\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_{11}\bar{\mathbf{A}}_{kl}^{-1})_{\alpha\beta}. \tag{B11}$$

After some transformations we obtain

$$\frac{\partial\langle\phi_k|r_1^{-q}|\phi_l\rangle}{\partial(\bar{\mathbf{A}}_{kl})_{\alpha\beta}} = -\langle\phi_k|r_1^{-q}|\phi_l\rangle\left[\frac{m_{mk}-q}{2}\mathrm{tr}^{-1}(\bar{\mathbf{J}}_{11}\bar{\mathbf{A}}_{kl}^{-1})\times(\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_{11}\bar{\mathbf{A}}_{kl}^{-1})_{\alpha\beta}+\frac{1}{2}(\bar{\mathbf{A}}_{kl}^{-1})_{\alpha\beta}\right] \tag{B12}$$

and

$$\langle\phi_k|r_1^{-q}\mathbf{r}'\bar{\mathbf{B}}\mathbf{r}|\phi_l\rangle = \tfrac{1}{2}\langle\phi_k|r_1^{-q}|\phi_l\rangle[3\,\mathrm{tr}(\mathbf{A}_{kl}^{-1}\mathbf{B})+(m_{kl}-q)\times(\mathbf{A}_{kl}^{-1})_{11}^{-1}(\mathbf{A}_{kl}^{-1}\mathbf{B}\mathbf{A}_{kl}^{-1})_{11}]. \tag{B13}$$

3. Integral $\langle\phi_k|r_1^{-q}\mathbf{r}'\bar{\mathbf{B}}\mathbf{r}\mathbf{r}'\bar{\mathbf{C}}\mathbf{r}|\phi_l\rangle$

Similarly to (B8) we can write

$$\langle\phi_k|r_1^{-q}\mathbf{r}'\bar{\mathbf{B}}\mathbf{r}\mathbf{r}'\bar{\mathbf{C}}\mathbf{r}|\phi_l\rangle = \langle\phi_k|r_1^{-q}\mathbf{r}_\alpha\mathbf{r}_\beta\mathbf{r}_\rho\mathbf{r}_\gamma|\phi_l\rangle\bar{\mathbf{B}}^{\alpha\beta}\bar{\mathbf{C}}^{\rho\gamma}, \tag{B14}$$

which, combined with (A14), gives

$$\langle\phi_k|r_1^{-q}\mathbf{r}_\alpha\mathbf{r}_\beta\mathbf{r}_\rho\mathbf{r}_\gamma|\phi_l\rangle = \frac{\partial^2\langle\phi_k|r_1^{-q}|\phi_l\rangle}{\partial(\bar{\mathbf{A}}_{kl})_{\alpha\beta}\partial(\bar{\mathbf{A}}_{kl})_{\rho\gamma}}. \tag{B15}$$

In addition to some expressions derived above we also need the relation

$$\frac{\partial(\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_{11}\bar{\mathbf{A}}_{kl}^{-1})_{\alpha\beta}}{\partial(\bar{\mathbf{A}}_{kl}^{-1})_{\rho\gamma}} = -[(\bar{\mathbf{A}}_{kl}^{-1})_{\alpha\rho}(\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_{11}\bar{\mathbf{A}}_{kl}^{-1})_{\gamma\beta} + (\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_{11}\bar{\mathbf{A}}_{kl}^{-1})_{\alpha\rho}(\bar{\mathbf{A}}_{kl}^{-1})_{\gamma\beta}]. \tag{B16}$$

We use it to evaluate the following derivative

$$\frac{\partial^2\langle\phi_k|r_1^{-q}|\phi_l\rangle}{\partial(\bar{\mathbf{A}}_{kl})_{\rho\gamma}\partial(\bar{\mathbf{A}}_{kl})_{\alpha\beta}} = \frac{1}{4}\langle\phi_k|r_1^{-q}|\phi_l\rangle[(m_{kl}-q)(m_{kl}-q-2)\mathrm{tr}^{-2}[\bar{\mathbf{J}}_{11}\bar{\mathbf{A}}_{kl}^{-1}](\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_{11}\bar{\mathbf{A}}_{kl}^{-1})_{\alpha\beta}(\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_{11}\bar{\mathbf{A}}_{kl}^{-1})_{\rho\gamma}+(m_{kl}-q)\mathrm{tr}^{-1}[\bar{\mathbf{J}}_{11}\bar{\mathbf{A}}_{kl}^{-1}]$$
$$\times[(\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_{11}\bar{\mathbf{A}}_{kl}^{-1})_{\alpha\beta}(\bar{\mathbf{A}}_{kl}^{-1})_{\rho\gamma}+(\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_{11}\bar{\mathbf{A}}_{kl}^{-1})_{\rho\gamma}(\bar{\mathbf{A}}_{kl}^{-1})_{\alpha\beta}]+2(m_{kl}-q)\mathrm{tr}^{-1}[\bar{\mathbf{J}}_{11}\bar{\mathbf{A}}_{kl}^{-1}][(\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_{11}\bar{\mathbf{A}}_{kl}^{-1})_{\gamma\beta}(\bar{\mathbf{A}}_{kl}^{-1})_{\alpha\rho}$$
$$+(\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_{11}\bar{\mathbf{A}}_{kl}^{-1})_{\alpha\rho}(\bar{\mathbf{A}}_{kl}^{-1})_{\gamma\beta}]+(\bar{\mathbf{A}}_{kl}^{-1})_{\alpha\beta}(\bar{\mathbf{A}}_{kl}^{-1})_{\rho\gamma}+2(\bar{\mathbf{A}}_{kl}^{-1})_{\alpha\rho}(\bar{\mathbf{A}}_{kl}^{-1})_{\gamma\beta}]. \tag{B17}$$

The final result is

$$\langle\phi_k|r_1^{-q}\mathbf{r}'\bar{\mathbf{B}}\mathbf{r}\mathbf{r}'\bar{\mathbf{C}}\mathbf{r}|\phi_l\rangle = \tfrac{1}{4}\langle\phi_k|r_1^{-q}|\phi_l\rangle[(m_{kl}-q)(m_{kl}-q-2)(\mathbf{A}_{kl}^{-1})_{11}^{-2}(\mathbf{A}_{kl}^{-1}\mathbf{B}\mathbf{A}_{kl}^{-1})_{11}(\mathbf{A}_{kl}^{-1}\mathbf{C}\mathbf{A}_{kl}^{-1})_{11} + 3(m_{kl}-q)$$
$$\times(\mathbf{A}_{kl}^{-1})_{11}^{-1}[(\mathbf{A}_{kl}^{-1}\mathbf{B}\mathbf{A}_{kl}^{-1})_{11}\,\mathrm{tr}[\mathbf{A}_{kl}^{-1}\mathbf{C}] + (\mathbf{A}_{kl}^{-1}\mathbf{C}\mathbf{A}_{kl}^{-1})_{11}\,\mathrm{tr}[\mathbf{A}_{kl}^{-1}\mathbf{B}]] + 2(m_{kl}-q)(\mathbf{A}_{kl}^{-1})_{11}^{-1}[(\mathbf{A}_{kl}^{-1}\mathbf{B}\mathbf{A}_{kl}^{-1}\mathbf{C}'\mathbf{A}_{kl}^{-1})_{11}$$
$$+ (\mathbf{A}_{kl}^{-1}\mathbf{B}'\mathbf{A}_{kl}^{-1}\mathbf{C}\mathbf{A}_{kl}^{-1})_{11}] + 9\,\mathrm{tr}[\mathbf{A}_{kl}^{-1}\mathbf{B}]\mathrm{tr}[\mathbf{A}_{kl}^{-1}\mathbf{C}] + 6\,\mathrm{tr}[\mathbf{A}_{kl}^{-1}\mathbf{B}\mathbf{A}_{kl}^{-1}\mathbf{C}']]. \tag{B18}$$

APPENDIX C: DARWIN TERM

In the first approach based on the $\hat{H}_{\mathrm{D}}^{I}(\mathbf{r})$ Hamiltonian the matrix element to calculate is

$$\langle\phi_k|\hat{H}_{\mathrm{D}}^{I}|\phi_l\rangle = \frac{\alpha^2}{8}\left[\sum_{i=1}^{n} q_0 q_i\left(\frac{1}{M_1^2}+\frac{1}{M_{i+1}^2}\right)\left(\left\langle\nabla_{\mathbf{r}}'\bar{\mathbf{J}}_{ii}\nabla_{\mathbf{r}}\phi_k\middle|\frac{1}{r_i}\middle|\phi_l\right\rangle + \left\langle\phi_k\middle|\frac{1}{r_i}\middle|\nabla_{\mathbf{r}}'\bar{\mathbf{J}}_{ii}\nabla_{\mathbf{r}}\phi_l\right\rangle + 2\left\langle\bar{\mathbf{J}}_{ii}\nabla_{\mathbf{r}}\phi_k\middle|\frac{1}{r_i}\middle|\bar{\mathbf{J}}_{ii}\nabla_{\mathbf{r}}\phi_l\right\rangle\right)\right.$$
$$\left.+\sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{q_i q_j}{M_{i+1}^2}\left(\left\langle\nabla_{\mathbf{r}}'\bar{\mathbf{J}}_{ii}\nabla_{\mathbf{r}}\phi_k\middle|\frac{1}{r_{ij}}\middle|\phi_l\right\rangle + \left\langle\phi_k\middle|\frac{1}{r_{ij}}\middle|\nabla_{\mathbf{r}}'\bar{\mathbf{J}}_{ii}\nabla_{\mathbf{r}}\phi_l\right\rangle + 2\left\langle\bar{\mathbf{J}}_{ii}\nabla_{\mathbf{r}}\phi_k\middle|\frac{1}{r_{ij}}\middle|\bar{\mathbf{J}}_{ii}\nabla_{\mathbf{r}}\phi_l\right\rangle\right)\right]. \tag{C1}$$

In the second approach ($H_{\mathrm{D}}^{II}(\mathbf{r})$) the following matrix element that needs to be calculated is

$$\langle\phi_k|\hat{H}_{\mathrm{D}}^{II}|\phi_l\rangle = -\frac{\pi\alpha^2}{2}\left[\sum_{i=1}^{n}\left(\frac{1}{M_1^2}+\frac{1}{M_{i+1}^2}\right)q_0 q_i\langle\phi_k|\delta(\mathbf{r}_i)|\phi_l\rangle\right.$$
$$\left.+\sum_{i=1}^{n}\sum_{j=1,j\neq i}^{n}\frac{1}{M_{i+1}^2}q_i q_j\langle\phi_k|\delta(\mathbf{r}_{ij})|\phi_l\rangle\right]. \tag{C2}$$

APPENDIX D: DARWIN CORRECTION: THE FIRST APPROACH

In the expression for the matrix element involving the $\hat{H}_{\mathrm{D}}^{I}(\mathbf{r})$ operator the following sum of integrals appears:

$$\langle\phi_k|\hat{H}_{\mathrm{D}}^{I}|\phi_l\rangle = \left\langle\nabla_{\mathbf{r}}'\bar{\mathbf{J}}_{ii}\nabla_{\mathbf{r}}\phi_k\middle|\frac{1}{r_g}\middle|\phi_l\right\rangle + \left\langle\phi_k\middle|\frac{1}{r_g}\middle|\nabla_{\mathbf{r}}'\bar{\mathbf{J}}_{ii}\nabla_{\mathbf{r}}\phi_l\right\rangle + 2\left\langle\bar{\mathbf{J}}_{ii}\nabla_{\mathbf{r}}\phi_k\middle|\frac{1}{r_g}\middle|\bar{\mathbf{J}}_{ii}\nabla_{\mathbf{r}}\phi_l\right\rangle, \tag{D1}$$

where g stands for either i or ij.

Using (A4) and (A6) and simplifying the resulting expression, we obtain

$$\left\langle\nabla_{\mathbf{r}}'\bar{\mathbf{J}}_{ii}\nabla_{\mathbf{r}}\phi_k\middle|\frac{1}{r_g}\middle|\phi_l\right\rangle + \left\langle\phi_k\middle|\frac{1}{r_g}\middle|\nabla_{\mathbf{r}}'\bar{\mathbf{J}}_{ii}\nabla_{\mathbf{r}}\phi_l\right\rangle + 2\left\langle\bar{\mathbf{J}}_{ii}\nabla_{\mathbf{r}}\phi_k\middle|\frac{1}{r_g}\middle|\bar{\mathbf{J}}_{ii}\nabla_{\mathbf{r}}\phi_l\right\rangle =$$
$$-6(\mathbf{A}_{kl})_{ii}\left\langle\phi_k\middle|\frac{1}{r_g}\middle|\phi_l\right\rangle + 4\left\langle\phi_k\middle|\frac{1}{r_g}\mathbf{r}'\bar{\mathbf{A}}_{kl}\bar{\mathbf{J}}_{ii}\bar{\mathbf{A}}_{kl}\mathbf{r}\phi_l\right\rangle$$
$$+\delta_{i1}m_{kl}(m_{kl}+1)\left\langle\phi_k\middle|r_1^{-2}\frac{1}{r_g}\middle|\phi_l\right\rangle$$
$$-2\delta_{i1}m_{kl}\left\langle\phi_k\middle|r_1^{-2}\frac{1}{r_g}\mathbf{r}'(\bar{\mathbf{A}}_{kl}\bar{\mathbf{J}}_{11}+\bar{\mathbf{J}}_{11}\bar{\mathbf{A}}_{kl})\mathbf{r}\middle|\phi_l\right\rangle.$$

To complete the above formula we need to determine the following four integrals:

$$\left\langle\phi_k\middle|\frac{1}{r_g}\middle|\phi_l\right\rangle,\quad \left\langle\phi_k\middle|r_1^{-2}\frac{1}{r_g}\middle|\phi_l\right\rangle,\quad \left\langle\phi_k\middle|\frac{1}{r_g}\mathbf{r}'\bar{\mathbf{B}}\mathbf{r}\middle|\phi_l\right\rangle,$$

$$\left\langle\phi_k\middle|r_1^{-2}\frac{1}{r_g}\mathbf{r}'\bar{\mathbf{B}}\mathbf{r}\middle|\phi_l\right\rangle.$$

In the expressions we derive next we use the following notation:

$$\bar{a} = \mathrm{tr}[\bar{\mathbf{J}}_{11}\bar{\mathbf{A}}_{kl}^{-1}],\quad a = \mathrm{tr}[\mathbf{J}_{11}\mathbf{A}_{kl}^{-1}], \tag{D2}$$

$$\bar{b} = \mathrm{tr}[\bar{\mathbf{J}}_{g}\bar{\mathbf{A}}_{kl}^{-1}],\quad b = \mathrm{tr}[\mathbf{J}_{g}\mathbf{A}_{kl}^{-1}], \tag{D3}$$

$$\bar{c} = \mathrm{tr}[\bar{\mathbf{J}}_{11}\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_{g}\bar{\mathbf{A}}_{kl}^{-1}],\quad c = \mathrm{tr}[\mathbf{J}_{11}\mathbf{A}_{kl}^{-1}\mathbf{J}_{g}\mathbf{A}_{kl}^{-1}], \tag{D4}$$

$$\gamma_2(q) = \frac{\Gamma[q+1]}{\Gamma[q+3/2]}, \tag{D5}$$

$$\gamma_3(q) = \frac{\Gamma[q+1/2]}{\Gamma[q+1]\Gamma[1/2]}, \tag{D6}$$

where matrix $\mathbf{J}_g$ for $g=\{i\}$ becomes $\mathbf{J}_{ii}$ and for $g=\{ij\}$ becomes $\mathbf{J}_{ij}$.

1. Integral $\langle\phi_k|r_1^{-q}(1/r_g)|\phi_l\rangle$

From (A10) we have

$$\left\langle \phi_k \left| r_1^{-q} \frac{1}{r_g} \right| \phi_l \right\rangle = \frac{2}{\sqrt{\pi}} (-)^p \frac{\partial^p}{\partial u^p} \int_0^\infty \int_{-\infty}^\infty \exp[-\mathbf{r}'(\bar{\mathbf{A}}_{kl} + u\bar{\mathbf{J}}_{11} + t^2\bar{\mathbf{J}}_g)\mathbf{r}] d\mathbf{r} dt_{u=0}$$

$$= \frac{2}{\sqrt{\pi}} (-)^p \frac{\partial^p}{\partial u^p} \int_0^\infty \pi^{3n/2} |\mathbf{A}_{kl} + u\mathbf{J}_{11} + t^2\mathbf{J}_g|^{-3/2}\, dt|_{u=0} = \frac{2}{\sqrt{\pi}} (-)^p \langle f_k | f_l \rangle \frac{\partial^p}{\partial u^p} \int_0^\infty |\mathbf{I}_n + u\mathbf{J}_{11}\mathbf{A}_{kl}^{-1} + t^2\mathbf{J}_g\mathbf{A}_{kl}^{-1}|^{-3/2}\, dt|_{u=0}. \tag{D7}$$

Using (A16) and definitions (D2)–(D4) one obtains

$$|\mathbf{I}_n + u\mathbf{J}_{11}\mathbf{A}_{kl}^{-1} + t^2\mathbf{J}_g\mathbf{A}_{kl}^{-1}| = 1 + ua + t^2 b + ut^2(ab - c) \tag{D8}$$

and

$$\int_0^\infty [1 + ua + t^2 b + ut^2(ab - c)]^{-3/2} dt = (1 + au)^{-1}[b + u(ab - c)]^{-1/2}. \tag{D9}$$

Now using the Leibniz formula (A17) one may evaluate the following derivatives:

$$\frac{\partial^{p-s}}{\partial u^{p-s}} (1 + au)^{-1}|_{u=0} = (-)^{p-s}\Gamma[p - s + 1] a^{p-s}, \tag{D10}$$

$$\frac{\partial^s}{\partial u^s} (b + u(ab - c))^{-1/2}|_{u=0} = (-)^s \frac{\Gamma[s + 1/2]}{\Gamma[1/2]} \left(1 - \frac{c}{ab}\right)^s \frac{a^s}{\sqrt{b}}, \tag{D11}$$

and

$$\frac{\partial^s}{\partial u^s} (1 + au)^{-1}[b + u(ab - c)]^{-1/2}|_{u=0} = (-)^p \Gamma[p + 1] \frac{a^p}{\sqrt{\pi}} \sum_{s=0}^{p} \gamma_3(s) \left(1 - \frac{c}{ab}\right)^s. \tag{D12}$$

With the expression for $\langle \phi_k | r_1^{-q} | \phi_l \rangle$ (B4),

$$\frac{2}{\pi} \langle f_k | f_l \rangle a^p = \frac{\langle \phi_k | r_1^{-q} | \phi_l \rangle}{\Gamma[p + 3/2]}, \tag{D13}$$

we obtain the following final expression for the integral $\langle \phi_k | r_1^{-q} (1/r_g) | \phi_l \rangle$:

$$\left\langle \phi_k \left| r_1^{-q} \frac{1}{r_g} \right| \phi_l \right\rangle = \langle \phi_k | r_1^{-q} | \phi_l \rangle \frac{\gamma_2(p)}{\sqrt{b}} \sum_{s=0}^{p} \gamma_3(s) \left(1 - \frac{c}{ab}\right)^s. \tag{D14}$$

2. Integral $\langle \phi_k | r_1^{-q} (1/r_g) \mathbf{r}' \bar{\mathbf{B}} \mathbf{r} | \phi_l \rangle$

We first need to calculate the following derivative:

$$\frac{\partial \langle \phi_k | r_1^{-q} (1/r_g) | \phi_l \rangle}{\partial (\bar{\mathbf{A}}_{kl})_{\alpha\beta}} = -\left\langle \phi_k \left| r_1^{-q} \frac{1}{r_g} \mathbf{r}_\alpha \mathbf{r}_\beta \right| \phi_l \right\rangle. \tag{D15}$$

Using the previously determined derivatives and the following derivative:

$$\frac{\partial \bar{c}}{\partial (\bar{\mathbf{A}}_{kl})_{\alpha\beta}} = \frac{\partial \,\mathrm{tr}[\bar{\mathbf{J}}_{11}\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_g\bar{\mathbf{A}}_{kl}^{-1}]}{\partial (\bar{\mathbf{A}}_{kl})_{\alpha\beta}} = -[(\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_{11}\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_g)_{\alpha\beta} + (\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_g\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_{11})_{\alpha\beta}], \tag{D16}$$

we have

$$\frac{\partial \langle \phi_k | r_1^{-q} (1/r_g) | \phi_l \rangle}{\partial (\bar{\mathbf{A}}_{kl})_{\alpha\beta}} = -\frac{1}{2}\left\langle \phi_k \left| r_1^{-q} \frac{1}{r_g} \right| \phi_l \right\rangle \left[2\frac{p}{\bar{a}} (\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_{11}\bar{\mathbf{A}}_{kl}^{-1})_{\alpha\beta} + (\bar{\mathbf{A}}_{kl}^{-1})_{\alpha\beta} - \frac{1}{\bar{b}} (\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_g\bar{\mathbf{A}}_{kl}^{-1})_{\alpha\beta} \right]$$

$$+ \langle \phi_k | r_1^{-q} | \phi_l \rangle \frac{3\sqrt{3}\gamma_2(p)}{\bar{a}^2\bar{b}^2\sqrt{\bar{b}}} \sum_{s=1}^{p} \gamma_3(s) s \left(1 - \frac{3\bar{c}}{\bar{a}\bar{b}}\right)^{s-1} \times [\bar{a}\bar{b}(\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_{11}\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_g\bar{\mathbf{A}}_{kl}^{-1})_{\alpha\beta} + \bar{a}\bar{b}(\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_g\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_{11}\bar{\mathbf{A}}_{kl}^{-1})_{\alpha\beta}$$

$$- \bar{a}\bar{c}(\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_g\bar{\mathbf{A}}_{kl}^{-1})_{\alpha\beta} - \bar{b}\bar{c}(\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_{11}\bar{\mathbf{A}}_{kl}^{-1})_{\alpha\beta}]. \tag{D17}$$

Using the above we obtain the final expression for the $\langle \phi_k | r_1^{-q} (1/r_g) \mathbf{r}' \bar{\mathbf{B}} \mathbf{r} | \phi_l \rangle$ integral,

$$\left\langle \phi_k \left| r_1^{-q} \frac{1}{r_g} \mathbf{r}' \bar{\mathbf{B}} \mathbf{r} \right| \phi_l \right\rangle = \frac{1}{2}\left\langle \phi_k \left| r_1^{-q} \frac{1}{r_g} \right| \phi_l \right\rangle \left[\frac{m_{kl} - q}{a} (\mathbf{A}_{kl}^{-1}\mathbf{B}\mathbf{A}_{kl}^{-1})_{11} + 3\,\mathrm{tr}[\mathbf{A}_{kl}^{-1}\mathbf{B}] - \frac{1}{b}\mathrm{tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_g\mathbf{A}_{kl}^{-1}\mathbf{B}] \right]$$

$$- \langle \phi_k | r_1^{-q} | \phi_l \rangle \frac{\gamma_2[(m_{kl} - q)/2]}{a^2 b^2 \sqrt{b}} \sum_{s=1}^{(m_{kl}-q)/2} \gamma_3(s) s \left(1 - \frac{c}{ab}\right)^{s-1} \times [ab(\mathbf{A}_{kl}^{-1}\mathbf{B}\mathbf{A}_{kl}^{-1}\mathbf{J}_g\mathbf{A}_{kl}^{-1})_{11}$$

$$+ ab(\mathbf{A}_{kl}^{-1}\mathbf{J}_g\mathbf{A}_{kl}^{-1}\mathbf{B}\mathbf{A}_{kl}^{-1})_{11} - ac\,\mathrm{tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_g\mathbf{A}_{kl}^{-1}\mathbf{B}] - bc(\mathbf{A}_{kl}^{-1}\mathbf{B}\mathbf{A}_{kl}^{-1})_{11}]. \tag{D18}$$

APPENDIX E: DARWIN CORRECTION: THE SECOND APPROACH

In the expression for the matrix element involving the $\hat{H}_{\mathrm{D}}^{II}$ operator the following integrals need to be evaluated:

$$\langle\phi_k|\hat{H}_{\mathrm{D}}^{II}|\phi_l\rangle = -\frac{\pi}{2c^2}\left[\sum_{i=1}^{n}\left(\frac{1}{M_1^2}+\frac{1}{M_{i+1}^2}\right)q_0 q_i\langle\phi_k|\delta(\mathbf{r}_i)|\phi_l\rangle + \sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{1}{M_{i+1}^2}q_i q_j\langle\phi_k|\delta(\mathbf{r}_{ij})|\phi_l\rangle\right]. \tag{E1}$$

To evaluate the above formula we need to determine the following integrals:

$$\langle\phi_k|\delta(\mathbf{r}_i)|\phi_l\rangle, \quad \langle\phi_k|\delta(\mathbf{r}_{ij})|\phi_l\rangle.$$

1. Integral $\langle\phi_k|\delta(\mathbf{r}_1)|\phi_l\rangle$

The integral has the following form:

$$\langle\phi_k|\delta(\mathbf{r}_i)|\phi_l\rangle = \int_{-\infty}^{\infty} r_1^{m_k+m_l}\exp[-\mathbf{r}'\bar{\mathbf{A}}_{kl}\mathbf{r}]\delta(\mathbf{r}_i)d\mathbf{r}.$$

Since for an arbitrary function $F(x)$,

$$\int_{-\infty}^{\infty} F(x)\,\delta(x)dx = F(0),$$

we have

- if $i=1$,

$$\langle\phi_k|\delta(\mathbf{r}_1)|\phi_l\rangle = \int_{-\infty}^{\infty} r_1^{m_{kl}}\exp[-\mathbf{r}'\bar{\mathbf{A}}_{kl}\mathbf{r}]\delta(\mathbf{r}_1)d\mathbf{r} \neq 0 \Leftrightarrow m_{kl}=0,$$

- if $i\neq 1$,

$$\langle\phi_k|\delta(\mathbf{r}_i)|\phi_l\rangle = \int_{-\infty}^{\infty} r_1^{m_{kl}}\exp[-\mathbf{r}'\bar{\mathbf{A}}_{kl}\mathbf{r}]\delta(\mathbf{r}_i)d\mathbf{r} \neq 0 \Leftrightarrow \text{for any } m_{kl}.$$

The matrix element of the Dirac delta function with simple spherical Gaussians can be obtained using the Gaussian representation of the delta function,[15]

$$\delta(\mathbf{r}_1-\boldsymbol{\xi}) = \lim_{s\to\infty}\left(\frac{s}{\pi}\right)^{3/2}\exp[-s(\mathbf{r}_1-\boldsymbol{\xi})^2]. \tag{E2}$$

With this,

$$\langle f_k|\delta(\mathbf{r}_1-\boldsymbol{\xi})|f_l\rangle = \lim_{s\to\infty}\left(\frac{s}{\pi}\right)^{3/2}\langle f_k|\exp[-sr_1^2 + 2s\mathbf{r}_1'\boldsymbol{\xi}-s\xi^2]|f_l\rangle. \tag{E3}$$

If j_1 is an n-component vector whose first element is equal to 1 and the rest are zeros, then

$$\langle f_k|\delta(\mathbf{r}_1-\boldsymbol{\xi})|f_l\rangle = \lim_{s\to\infty}\left(\frac{s}{\pi}\right)^{3/2}\exp[-s\xi^2]\langle f_k|\exp[-s\mathbf{r}'\bar{\mathbf{J}}_{11}\mathbf{r}+2s(j_1\otimes\boldsymbol{\xi})'\mathbf{r}]|f_l\rangle = \lim_{s\to\infty}\left(\frac{s}{\pi}\right)^{3/2}\exp[-s\xi^2]\int_{-\infty}^{\infty}\exp[-\mathbf{r}'(s\bar{\mathbf{J}}_{11} + \bar{\mathbf{A}}_{kl})\mathbf{r}+2s(j_1\otimes\boldsymbol{\xi})'\mathbf{r}]d\mathbf{r} = \lim_{s\to\infty}\left(\frac{s}{\pi}\right)^{3/2}\exp[-s\xi^2]\left[\frac{\pi^n}{|\mathbf{A}_{kl}+s\mathbf{J}_{11}|}\right]^{3/2}\exp[s^2(j_1\otimes\boldsymbol{\xi})'[\bar{\mathbf{A}}_{kl}+s\bar{\mathbf{J}}_{11}]^{-1}(j_1\otimes\boldsymbol{\xi})]. \tag{E4}$$

In the last expression we used the relation

$$\int_{-\infty}^{\infty}\exp[-\mathbf{r}'\bar{\mathbf{B}}\mathbf{r}+\mathbf{y}'\mathbf{r}]d\mathbf{r} = \left[\frac{\pi^n}{|\mathbf{B}|}\right]^{3/2}\exp\left[\frac{1}{4}\mathbf{y}'\bar{\mathbf{B}}^{-1}\mathbf{y}\right].$$

We can rewrite the determinant $|\mathbf{A}_{kl}+s\mathbf{J}_{11}|$ as

$$|\mathbf{A}_{kl}+s\mathbf{J}_{11}| = |\mathbf{A}_{kl}||\mathbf{I}_n+s\mathbf{J}_{11}\mathbf{A}_{kl}^{-1}| = |\mathbf{A}_{kl}|(1+s\,\mathrm{tr}[\mathbf{J}_{11}\mathbf{A}_{kl}^{-1}]).$$

Then,

$$\langle f_k|\delta(\mathbf{r}_1-\boldsymbol{\xi})|f_l\rangle = \left[\frac{\pi^{n-1}}{|\mathbf{A}_{kl}|}\right]^{3/2}\lim_{s\to\infty}\left[\frac{1}{1/s+\mathrm{tr}[\mathbf{J}_{11}\mathbf{A}_{kl}^{-1}]}\right]^{3/2} \times\exp[s^2(j_1\otimes\boldsymbol{\xi})'[\bar{\mathbf{A}}_{kl}+s\bar{\mathbf{J}}_{11}]^{-1} \times(j_1\otimes\boldsymbol{\xi})-s\xi^2]. \tag{E5}$$

Since the limit of the preexponential part of (E5) is a finite number, the limit of the exponent must be equal to $-\beta\xi^2$ with β being a finite number. Otherwise the entire expression (E5) would have been either zero or infinity, which is not the case. Hence,

$$\langle f_k|\delta(\mathbf{r}_1-\boldsymbol{\xi})|f_l\rangle = \left[\frac{\pi^{n-1}}{|\mathbf{A}_{kl}|}\right]^{3/2}\frac{1}{\mathrm{tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{11}]^{3/2}}\exp[-\beta\xi^2] = \langle f_k|f_l\rangle\frac{1}{\pi^{3/2}}\frac{1}{\mathrm{tr}[A_{kl}^{-1}J_{11}]^{3/2}}\exp[-\beta\xi^2]. \tag{E6}$$

Making use of the normalization condition,

$$\int_{-\infty}^{\infty} \langle f_k|\delta(\mathbf{r}_1-\boldsymbol{\xi})|f_l\rangle d\xi = \langle f_k|f_l\rangle, \tag{E7}$$

we find that $\beta=\mathrm{tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{11}]^{-1}$. Thus,

$$\langle f_k|\delta(\mathbf{r}_1-\boldsymbol{\xi})|f_l\rangle = \langle f_k|f_l\rangle \frac{1}{\pi^{3/2}} \frac{1}{\mathrm{tr}[A_{kl}^{-1}J_{11}]^{3/2}} \times \exp\left[-\frac{\xi^2}{\mathrm{tr}[A_{kl}^{-1}J_{11}]}\right]. \tag{E8}$$

The last relationship is now used to evaluate the matrix element $\langle\phi_k|\delta(\mathbf{r}_1-\boldsymbol{\xi})|\phi_l$. To do that we define $p=m_{kl}/2$ and according to (A8) we obtain

$$\begin{aligned}
&\langle\phi_k|\delta(\mathbf{r}_1-\boldsymbol{\xi})|\phi_l\rangle \\
&= \langle f_k|r_1^{2p}\delta(\mathbf{r}_1-\boldsymbol{\xi})|f_l\rangle = (-1)^p \frac{\partial^p}{\partial u^p}\langle f_k| \\
&\times \exp[-u\mathbf{r}'\bar{\mathbf{J}}_{11}\mathbf{r}]\delta(\mathbf{r}_1-\boldsymbol{\xi})|f_l\rangle|_{u=0} \\
&= (-1)^p \frac{\partial^p}{\partial u^p} \frac{\pi^{3n/2}}{|\mathbf{A}_{kl}+u\mathbf{J}_{11}|^{3/2}} \\
&\times \frac{1}{\pi^{3/2}} \frac{1}{\mathrm{tr}[(\mathbf{A}_{kl}+u\mathbf{J}_{11})^{-1}\mathbf{J}_{11}]^{3/2}} \\
&\times \exp\left[-\frac{\xi^2}{\mathrm{tr}[(\mathbf{A}_{kl}+u\mathbf{J}_{11})^{-1}\mathbf{J}_{11}]}\right]\Bigg|_{u=0}.
\end{aligned} \tag{E9}$$

Applying the following formulas:

$$\frac{\partial}{\partial u}|\mathbf{A}_{kl}+u\mathbf{J}_{11}| = |\mathbf{A}_{kl}+s\mathbf{J}_{11}|\mathrm{tr}[(\mathbf{A}_{kl}+s\mathbf{J}_{11})^{-1}\mathbf{J}_{11}], \tag{E10}$$

$$\frac{\partial}{\partial u}\mathrm{tr}[(\mathbf{A}_{kl}+u\mathbf{J}_{11})^{-1}\mathbf{J}_{11}] = -\mathrm{tr}[(\mathbf{A}_{kl}+u\mathbf{J}_{11})^{-1} \times \mathbf{J}_{11}(\mathbf{A}_{kl}+u\mathbf{J}_{11})^{-1}\mathbf{J}_{11}], \tag{E11}$$

and using $\mathrm{tr}[\mathbf{X}\mathbf{J}_{11}\mathbf{X}\mathbf{J}_{11}]=\mathrm{tr}[\mathbf{X}\mathbf{J}_{11}]^2=(\mathbf{X}_{11})^2$ for an arbitrary matrix $\mathbf{X}$ lead to the final result,

$$\langle\phi_k|\delta(\mathbf{r}_1-\boldsymbol{\xi})|\phi_l\rangle = \langle f_k|f_l\rangle \frac{1}{2\pi}\frac{1}{\Gamma[p+3/2]}\frac{1}{(\mathbf{A}_{kl}^{-1})_{11}^{3/2}} \times \left[\frac{\xi^2}{(\mathbf{A}_{kl}^{-1})_{11}}\right]^p \exp\left[-\frac{\xi^2}{(\mathbf{A}_{kl}^{-1})_{11}}\right]. \tag{E12}$$

In the above expression we used the following:

$$\langle\phi_k|\phi_l\rangle = \langle f_k|r_1^{2p}|f_l\rangle = \frac{2}{\sqrt{\pi}}\Gamma[p+3/2](\mathbf{A}_{kl}^{-1})_{11}^p\langle f_k|f_l\rangle. \tag{E13}$$

So if we put $\xi=0$ and $p=0$, we have

$$\langle\phi_k|\delta(\mathbf{r}_1-\boldsymbol{\xi})|\phi_l\rangle = \langle f_k|f_l\rangle \frac{1}{2\pi}\frac{1}{\Gamma[p+3/2]}\frac{1}{(\mathbf{A}_{kl}^{-1})_{11}^{3/2}}. \tag{E14}$$

2. Integral $\langle\phi_k|\delta(\mathbf{r}_{ij})|\phi_l\rangle$

The matrix elements of $\delta(\mathbf{r}_{ij})$ can be obtained by straightforward integration. The procedure is very similar to the evaluation of the overlap integral and yields

$$\begin{aligned}
\langle\phi_k|\delta(\mathbf{r}_{ij})|\phi_l\rangle &= \frac{2}{\sqrt{\pi}}\Gamma[p+3/2](\mathbf{D}_{kl}^{-1})_{11}^p\left[\frac{\pi^{n-1}}{|\mathbf{D}_{kl}|}\right]^{3/2} \\
&= \langle\phi_k|\phi_l\rangle\frac{1}{\pi^{3/2}}\left[\frac{|\mathbf{A}_{kl}|}{|\mathbf{D}_{kl}|}\right]^{3/2}\left[\frac{(\mathbf{D}_{kl}^{-1})_{11}}{(\mathbf{A}_{kl}^{-1})_{11}}\right]^p,
\end{aligned} \tag{E15}$$

where $\mathbf{D}_{kl}$ is an $(n-1)\times(n-1)$ matrix formed from $\mathbf{A}_{kl}$ by adding the jth row to the ith row, then adding the jth column to the ith column, and then crossing out the jth column and the jth row.

3. Integral $\langle\phi_k|\delta(\mathbf{r}_i)|\phi_l\rangle$

In the case of $\langle\phi_k|\delta(\mathbf{r}_i)|\phi_l\rangle$ we obtain the same expression as in (E15) but $\mathbf{D}_{kl}$ is formed from $\mathbf{A}_{kl}$ by crossing out the ith column and the ith row (without adding anything).

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