PHYSICAL REVIEW A **76**, 022512 (2007)

Improved calculations of the lowest vibrational transitions in HeH^+

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(Received 2 May 2007; published 30 August 2007)

More accurate variational calculations of the lowest three pure vibrational states ($v=0,1,2$) of the $^4HeH^+$ molecular ion have been carried out without assuming the Born-Oppenheimer approximation. In the calculations we included the complete set of α^2 relativistic corrections, i.e., mass-velocity, Darwin, spin-spin, and orbit-orbit. This allowed us to improve the agreement between the theory and the experiment for the vibrational frequencies of the $1\rightarrow 0$ and $2\rightarrow 1$ transitions as compared to our previous calculations [Stanke *et al.*, Phys. Rev. Lett. **96**, 233002 (2006)].

DOI: 10.1103/PhysRevA.76.022512 PACS number(s): 31.15.Pf, 31.10.+z, 31.25.Nj, 31.30.Jv

The helium hydride molecular ion, being formed out of two the most abundant elements in the universe, is an interesting system to study not only due to its simplicity but also because of its presence in interstellar molecular clouds. It has only two electrons like the hydrogen molecule, but it lacks inversion symmetry, making it easier to study by high-resolution ir spectroscopy. Due to the nonzero permanent dipole moment in HeH^+, it is possible to acquire very precise vibration-rotation and pure rotational transition frequencies for this system in the gas phase. Like the H_2 molecule, HeH^+ has long been a subject of experimental and theoretical studies (see, for example [1,2], and references therein). However, the vast majority of the theoretical studies of HeH^+ have so far been done within the Born-Oppenheimer framework and have not accounted for relativistic and/or QED corrections.

In our recent work [2] we reported very accurate, fully nonadiabatic, nonrelativistic calculations of the pure vibrational spectrum of HeH^+. The transition frequency reported there systematically overestimated the transition energies derived from the experiment. In an attempt to eliminate these discrepancies at least partially, in the following work [3] we carried out even more accurate calculations of the entire rovibrational spectrum of HeH^+ where we included the two largest relativistic corrections, i.e., the mass-velocity correction and the Darwin correction. Including these corrections noticeably improved the agreement between the theory and the experiment. In the present work we make an attempt to further improve the theory-experiment agreement by including in the calculated energies all remaining leading-order relativistic corrections in the calculations of the three lowest vibrational levels. The reason we focus only on the three lowest energy levels is because the transition frequencies between these levels have been experimentally determined with a very high precision. As the vibrational quantum number v increases, the experimental results for the transition frequencies become progressively less accurate, and this makes a meaningful comparison with the results of very accurate theoretical calculations almost impossible. In addition, the calculations of highly excited vibrational states also become somewhat less accurate than the calculations of the lower-lying states, because the nodal structure of their vibrational wave functions becomes more complicated. In order to achieve the same accuracy in the calculations of the highly excited states as for the ground state, one needs to use significantly more basis functions.

It should be mentioned that, although in this work we use some terms taken from the Born-Oppenheimer (BO) approximation (such as the vibrational quantum number v), we do not assume the separability of the motions of the heavy particles (nuclei) and the light particles (electrons). The use of the BO terminology is done solely for the purpose of better relating our results to the experiment and to avoid confusion.

In the non-BO calculations HeH^+ is a four-particle problem. In general, let us denote their masses as M_i and their charges as Q_i. We will assume that particle 1 is a ^{4}He nucleus (α particle), particle 2 is a ^{1}He nucleus (proton), and particles 3 and 4 are electrons. If the positions of the particles in the laboratory Cartesian coordinate system are denoted as $\mathbf{R}_i$, the HeH^+ nonrelativistic Hamiltonian in atomic units is

$$\hat{H}^{\mathrm{lab}}_{\mathrm{nonrel}} = -\sum_{i=1}^{4}\frac{1}{2M_i}\nabla^2_{\mathbf{R}_i} + \sum_{i=1}^{4}\sum_{j>i}^{4}\frac{Q_iQ_j}{R_{ij}}. \tag{1}$$

Since the relativistic corrections are small in HeH^+, it is possible to include them as perturbations. In this case, the total Hamiltonian of the system is a sum of the nonrelativistic Hamiltonian and a small relativistic correction:

$$\hat{H}^{\mathrm{lab}}_{\mathrm{tot}} = \hat{H}^{\mathrm{lab}}_{\mathrm{nonrel}} + \alpha^2\hat{H}^{\mathrm{lab}}_{\mathrm{rel}}. \tag{2}$$

Here α is the fine structure constant. $\hat{H}^{\mathrm{lab}}_{\mathrm{rel}}$ contains several terms, i.e., the so-called mass-velocity, Darwin, spin-spin, and orbit-orbit Hamiltonians. The spin-orbit interaction is not considered in this work since we only study states with a zero angular momentum, for which this interaction vanishes. The explicit form of the relativistic Hamiltonians in the laboratory coordinate frame is the following:

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

$$\hat{H}_{\mathrm{D}}^{\mathrm{lab}} = -\frac{\pi}{2}\sum_{i=3}^{4}\sum_{j=1,j\neq i}^{4}\frac{Q_iQ_j}{M_i^2}\delta(\mathbf{R}_{ij}), \tag{4}$$

$$\hat{H}_{\mathrm{OO}}^{\mathrm{lab}} = \frac{1}{2}\sum_{j=1}^{4}\sum_{i>j}^{4}\frac{Q_iQ_j}{M_iM_j}\left(\frac{1}{R_{ij}}\boldsymbol{\nabla}_{\mathbf{R}_i}'\boldsymbol{\nabla}_{\mathbf{R}_j} + \frac{1}{R_{ij}^3}\mathbf{R}_{ij}'(\mathbf{R}_{ij}'\boldsymbol{\nabla}_{\mathbf{R}_i})\boldsymbol{\nabla}_{\mathbf{R}_j}\right), \tag{5}$$

$$\hat{H}_{\mathrm{SS}}^{\mathrm{lab}} = -\frac{8\pi}{3}\sum_{i=3}^{4}\sum_{j>i}^{4}\frac{Q_iQ_j}{M_iM_j}\mathbf{S}_i'\mathbf{S}_j\delta(\mathbf{R}_{ij}) = 2\pi\frac{Q_3Q_4}{M_3M_4}\delta(\mathbf{R}_{34}). \tag{6}$$

In the above expressions we do not include the Darwin corrections for the nuclei since they are negligibly small. Also, we assume that the two electrons are in a singlet spin state.

In order to develop the framework for the non-BO calculation of internal stationary bound states of HeH^+, we first separate out the motion of the center of mass (we denote the center-of-mass coordinates in the laboratory coordinate system as $\mathbf{r}_0$). There are a number of ways the internal coordinates can be chosen. In our approach, as described in [4,5], we use the following internal coordinates:

$$\mathbf{r}_1 = -\mathbf{R}_1 + \mathbf{R}_2,$$

$$\mathbf{r}_2 = -\mathbf{R}_1 + \mathbf{R}_3,$$

$$\mathbf{r}_3 = -\mathbf{R}_1 + \mathbf{R}_4. \tag{7}$$

In the new coordinates, the nonrelativistic Hamiltonian has the following form:

$$\hat{H}_{\mathrm{nonrel}}^{\mathrm{int}} = -\frac{1}{2}\left(\sum_{i=1}^{3}\frac{1}{\mu_i}\nabla_{\mathbf{r}_i}^2 + \sum_{i=1}^{3}\sum_{j\neq i}^{3}\frac{1}{m_0}\boldsymbol{\nabla}_{\mathbf{r}_i}'\boldsymbol{\nabla}_{\mathbf{r}_j}\right) + \sum_{i=1}^{3}\frac{q_0q_i}{r_i} + \sum_{i<j}^{3}\frac{q_iq_j}{r_{ij}}, \tag{8}$$

where $r_{ij}=|\mathbf{r}_j-\mathbf{r}_i|$, $\mu_i=m_0m_i/(m_0+m_i)$, and $q_i=Q_{i+1}$, respectively. We also used the notation $m_i=M_{i+1}$. The quantities μ_i and q_i play the role of the masses and charges of the pseudoparticles moving in the field of the reference particle, which in our case is particle 1.

The transformation of the relativistic Hamiltonians (3)–(6) to the internal frame was described in [6,7]. The corresponding expressions are as follows:

$$\hat{H}_{\mathrm{MV}}^{\mathrm{int}} = -\frac{1}{8}\left[\frac{1}{m_0^3}\left(\sum_{i=1}^{3}\boldsymbol{\nabla}_{\mathbf{r}_i}\right)^4 + \sum_{i=1}^{3}\frac{1}{m_i^3}\nabla_{\mathbf{r}_i}^4\right], \tag{9}$$

$$\hat{H}_{\mathrm{D}}^{\mathrm{int}} = -\frac{\pi}{2}\left(\sum_{i=2}^{3}\frac{q_0q_i}{m_i^2}\delta(\mathbf{r}_i) + \sum_{i=2}^{3}\sum_{j\neq i}^{3}\frac{q_iq_j}{m_i^2}\delta(\mathbf{r}_{ij})\right), \tag{10}$$

$$\hat{H}_{\mathrm{OO}}^{\mathrm{int}} = -\frac{1}{2}\sum_{i=1}^{3}\sum_{j=1}^{3}\frac{q_0q_j}{m_0m_j}\left(\frac{1}{r_j}\boldsymbol{\nabla}_{\mathbf{r}_i}'\boldsymbol{\nabla}_{\mathbf{r}_j} + \frac{1}{r_j^3}\mathbf{r}_j'(\mathbf{r}_j'\boldsymbol{\nabla}_{\mathbf{r}_i})\boldsymbol{\nabla}_{\mathbf{r}_j}\right) + \frac{1}{2}\sum_{i=1}^{3}\sum_{j>i}^{3}\frac{q_iq_j}{m_im_j}\left(\frac{1}{r_{ij}}\boldsymbol{\nabla}_{\mathbf{r}_i}'\boldsymbol{\nabla}_{\mathbf{r}_j} + \frac{1}{r_{ij}^3}\mathbf{r}_{ij}'(\mathbf{r}_{ij}'\boldsymbol{\nabla}_{\mathbf{r}_i})\boldsymbol{\nabla}_{\mathbf{r}_j}\right), \tag{11}$$

$$\hat{H}_{\mathrm{SS}}^{\mathrm{int}} = 2\pi\frac{q_2q_3}{m_2m_3}\delta(\mathbf{r}_{23}). \tag{12}$$

It should be noted that, upon the transformation to the internal frame, the mass-velocity Hamiltonian, apart from a term only dependent on the center-of-mass coordinate $\mathbf{r}_0$, also includes a term that couples $\mathbf{r}_0$ with $\mathbf{r}_1$, $\mathbf{r}_2$, and $\mathbf{r}_3$. But, since we assume that the system as a whole is not moving, this coupling term can be set to zero.

In the first stage of the calculations we solve the nonrelativistic problem with Hamiltonian (8). In this, as in our previous studies [2,3], we use the variational method and we expand the wave function in terms of explicitly correlated Gaussian basis functions that contain premultipliers in the form of even powers of the internuclear distance:

$$\phi_k = r_1^{p_k}\exp[-\mathbf{r}'(A_k\otimes I_3)\mathbf{r}]. \tag{13}$$

$\mathbf{r}$ in the case of HeH^+ is a nine-component column vector,

$$\mathbf{r} = \begin{bmatrix}\mathbf{r}_1\\ \mathbf{r}_2\\ \mathbf{r}_3\end{bmatrix}, \tag{14}$$

A_k is a real, symmetric, positive definite 3×3 matrix of exponential parameters that are unique for each basis function, and I_3 is the 3×3 identity matrix. The prime and $\otimes$ signs denote the matrix or vector transposition and the Kronecker product, respectively.

From the computational point of view, it is convenient to represent the matrix A_k in the Cholesky-factored form, $A_k = L_kL_k'$. With such a representation, there are no constraints on the values of the elements of L_k, while the elements of the original A_k matrix must obey certain constraints to maintain the positive definiteness of the matrix. The range of the allowed powers p_k in our calculations on HeH^+ was 0–250. As our previous works have demonstrated, the basis functions (13) are capable of representing wave functions of diatomic systems with σ electrons very accurately.

To account for the permutational symmetry of the particles in HeH^+, one needs to apply certain projection operators to the basis functions (13). In the case when two electrons are in a singlet state (the ground electronic state of HeH^+ is $X\,{}^1\Sigma^+$) this operator is $1+\hat{P}_{34}$, where $\hat{P}_{34}$ is the permutation of the spatial coordinates of particles 3 and 4. The action of $\hat{P}_{34}$ on the basis functions is equivalent to a certain transformation of the matrix of the exponential parameters, A_k, and can be easily implemented in a computer code.

The masses of the nuclei that we used in the calculations were taken from the CODATA 2002 set of rec-

TABLE I. Total nonrelativistic energies, mass-velocity corrections (MV), Darwin corrections (D), and spin-spin corrections (SS), computed with a combined basis of 18 000 functions (13). All values are in a.u.

v	$E_{\rm nonrel}$	$\alpha^2\langle\hat{H}_{\rm MV}\rangle$	$\alpha^2\langle\hat{H}_{\rm D}\rangle$	$\alpha^2\langle\hat{H}_{\rm SS}\rangle$
0	−2.9710784657	-7.128024×10^{-4}	5.850925×10^{-4}	3.36711×10^{-5}
1	−2.9578148926	-7.111301×10^{-4}	5.833372×10^{-4}	3.34661×10^{-5}
2	−2.9459492590	-7.100812×10^{-4}	5.821123×10^{-4}	3.33563×10^{-5}

ommended values. The masses are as follows: $m_{\rm He}=7294.299\,536\,3$ a.u. (^{4}He isotope) and $m_{\rm H}=1836.152\,672\,61$ a.u. (proton).

In the present calculations we have generated a variational expansion consisting of 6000 basis functions (13) calculated independently for each of the considered vibrational states of HeH$^+$. The procedure used to select and optimize the exponential parameters of basis functions was similar to that used in previous works [2,3]. As a starting point for the calculations we took the 5400-term basis sets generated in [3]. Then we gradually increased the basis size for each state to 6000. It should be emphasized, however, that the gain achieved in the accuracy of the calculations was mainly due to more thorough optimization of the nonlinear exponential parameters of all basis functions and less due to the inclusion of additional functions in the basis set. With 6000 basis functions (13) we obtained the energy values of −2.971 078 464 64, −2.957 814 888 27, and −2.945 949 256 20 a.u. for $v=0$, 1, and 2 vibrational states, respectively. As was mentioned, each state was calculated independently, meaning that the optimization of the exponential parameters was done with respect to that particular state.

In general, any optimization of the exponential parameters is usually a very computationally costly procedure. In 6000 basis functions (13) for HeH$^+$ there are $6000\times6=36\,000$ exponential parameters. A "single-point" energy calculation requires a calculation of millions of matrix elements. In this respect, the use of the analytic gradient [4,5] is very helpful and allows a significant reduction in the computational cost of the variational minimization. After the number of basis functions reached 6000 for each state, we combined the three basis sets we obtained for the $v=0$, 1, and 2 states and formed a single basis set with 18 000 functions. With this basis set we recalculated all three states. We estimate that the combined basis set is equivalent to a fully optimized basis with approximately 6500-7000 basis functions for each state.

The total nonrelativistic energies computed with the combined basis of 18 000 functions are shown in Table I. These energies are noticeably lower than those obtained in our previous work [3], especially for the $v=2$ state. The ground-state nonrelativistic energy of −2.971 078 465 7 a.u. shown in Table I can be compared with the result of the recent highly accurate nonadiabatic calculation by Zhou *et al.* [8], where Hylleraas-type basis functions were used for expanding the wave function. The value reported in [8] of −2.971 078 469 6 a.u. is only by 4×10^{-9} a.u. lower than ours.

Next, we used the nonrelativistic wave functions to compute expectation values of the mass-velocity, Darwin, and spin-spin interaction Hamiltonians given by expressions (9), (10), and (12), respectively. The results are presented in Table I along with the nonrelativistic energies. To give a better idea how much these corrections contribute to the total relativistic energies (which were used later to determine the transition frequencies), we multiplied all of them by α^2. This also made it more convenient to compare the present results with those reported before [3].

The derivation of the $\hat{H}_{\rm MV}$, $\hat{H}_{\rm D}$, and $\hat{H}_{\rm SS}$ matrix elements with the basis functions (13) was presented before [6]. The evaluation of the matrix elements for the orbit-orbit interaction Hamiltonian (11) with basis functions (13) is significantly more involved than the evaluation of the other matrix elements. At the same time, the orbit-orbit contribution is the smallest of the four α^2 relativistic corrections. Thus, the required accuracy for determining this correction is not as high as for the others. For the purpose of this work it was sufficient to evaluate $\langle\hat{H}_{\rm OO}\rangle$ with three or four converged significant digits. For this reason we carried out the calculations of $\langle\hat{H}_{\rm OO}\rangle$ using wave functions obtained with a different basis set, which consisted of the following explicitly correlated complex Gaussian basis functions:

$$\begin{aligned}\phi_k &= \exp[-\mathbf{r}'(A_k\otimes I_3)\mathbf{r} - i\mathbf{r}'(B_k\otimes I_3)\mathbf{r}]\\ &= \exp[-\mathbf{r}'(C_k\otimes I_3)\mathbf{r}],\end{aligned} \tag{15}$$

where C_k is a complex symmetric matrix; A_k and B_k are the real and the imaginary parts of C_k, respectively. Such basis functions were considered by two of the present authors in [5]. The complex Gaussians are more flexible then the simple Gaussians (i.e., the Gaussians without premultipliers) with real exponential parameters and allow one not only to perform non-BO calculations on atomic systems, but also to calculate some molecular systems. Combined in pairs (or in larger groups), the complex Gaussians are capable of representing molecular non-BO wave functions whose "vibrational" components have maxima shifted away from the origin of the coordinate system while almost vanishing at the origin. However, in order to take full advantage of these features of the complex Gaussians one needs to perform a very costly optimization of their exponential parameters and, even then, the energy is usually not as good as what one gets with the same number of diatomic Gaussians (13). In fact, it is often very difficult to achieve in a calculation with complex Gaussians a relative accuracy that exceeds 10^{-5}–10^{-6}. Nonetheless, such an accuracy is satisfactory, if the only purpose of the calculation is to generate a wave function for computing the $\langle\hat{H}_{\rm OO}\rangle$ correction. We use complex Gaussians in calculating $\langle\hat{H}_{\rm OO}\rangle$ in this work because the matrix ele-

TABLE II. Total nonrelativistic energies and orbit-orbit corrections computed with basis functions (15). All values are in a.u.

Basis size	$E_{\text{nonrel}}(v=0)$	$E_{\text{nonrel}}(v=1)$	$E_{\text{nonrel}}(v=2)$	$\alpha^2\langle\hat{H}_{\text{OO}}\rangle(v=0)$	$\alpha^2\langle\hat{H}_{\text{OO}}\rangle(v=1)$	$\alpha^2\langle\hat{H}_{\text{OO}}\rangle(v=2)$
100	−2.970261	−2.955913	−2.942592	-7.6328×10^{-6}	-7.5383×10^{-6}	-7.4187×10^{-6}
200	−2.970916	−2.957464	−2.945324	-7.6294×10^{-6}	-7.5361×10^{-6}	-7.4478×10^{-6}
400	−2.971037	−2.957748	−2.945831	-7.6198×10^{-6}	-7.5190×10^{-6}	-7.4449×10^{-6}
1000	−2.971058	−2.957793	−2.945924	-7.6193×10^{-6}	-7.5163×10^{-6}	-7.4335×10^{-6}
3000, combined	−2.971071	−2.957804	−2.945931	-7.6185×10^{-6}	-7.5145×10^{-6}	-7.4342×10^{-6}

ments of the orbit-orbit Hamiltonian (11) with those functions are much simpler to evaluate than with the diatomic Gaussians (13) despite the fact that the exponential parameters are complex numbers in (15).

Using an increasingly larger number of complex Gaussians, we generated several non-BO wave functions for HeH^+ corresponding to the $v=0$, 1, and 2 states. The convergence of the nonrelativistic energies and of the expectation values of the orbit-orbit Hamiltonian obtained in the calculations is shown in Table II. The calculations were done independently for each vibrational state. The largest number of complex Gaussians used for each state was 1000. In the end we again combined the three basis sets to form a 3000-term set and with that set we recalculated the energy and $\langle\hat{H}_{\text{OO}}\rangle$ for each state. This provided an additional improvement to the results. The comparison of the nonrelativistic energies in Table II with more accurate values obtained with the diatomic Gaussians and presented in Table I shows the accuracy level of the calculations with the complex Gaussians. The complex Gaussian energies appear to be converged to five or six significant figures. The convergence of the orbit-orbit correction is somewhat worse, but we believe that four significant figures are accurate.

Now let us turn to the main point of this work, the calculation of the transition frequencies. In Table III we present a comparison of the theoretical 1 → 0 and 2 → 1 transition frequencies with the values derived from the experiment. In the table we also included the nonrelativistic frequencies obtained with the wave functions generated in this work, the frequencies that include only the mass-velocity and Darwin corrections (these frequencies were taken from our previous work [3]), and the frequencies that include all four α^2 relativistic corrections. For the experimental results we use the values obtained from the analytical fits generated based on the available microwave and infrared spectra with two different extrapolation methods [3]. As one can see, for both transitions, the accounting for the α^2 relativistic corrections brings the calculated transition frequencies very close to the experimental values, although some discrepancy of less than 0.02 cm^{-1} still remains. This discrepancy should probably be attributed to the radiative corrections (of the order of α^3 and higher) that were not computed in this work.

TABLE III. $v'\to v$ vibrational frequencies computed without inclusion of relativistic corrections, ΔE_{nonrel}, computed with inclusion of mass-velocity and Darwin corrections only, $\Delta E(\text{MV},\text{D})$, computed with inclusion of all relativistic corrections, $\Delta E(\text{MV},\text{D},\text{SS},\text{OO})$, in comparison with the frequencies extracted from experimental data by two different methods of extrapolation, ΔE^a_{expt} and ΔE^b_{expt}. All values are in cm^{-1}.

	1 → 0	2 → 1
ΔE_{nonrel}, this work	2911.0178	2604.2056
$\Delta E(\text{MV},\text{D})$ [3]	2911.0007	2604.1676
$\Delta E(\text{MV},\text{D},\text{SS},\text{OO})$, this work	2910.9774	2604.1604
ΔE^a_{expt} [3]	2910.9590	2604.1472
ΔE^b_{expt} [3]	2910.9572(7)	2604.1482(12)

Upon analyzing the relativistic contributions one can see that, for the first transition frequency (1 → 0), the inclusion of the spin-spin and orbit-orbit corrections has an even larger effect on the final result than the inclusion of the mass-velocity and Darwin corrections, even though in absolute terms the latter are larger by more than one order of magnitude. This situation is actually not totally surprising. As one can see from Tables I and II, the relativistic corrections have different signs and partially cancel each other. In particular, this cancellation occurs for the mass-velocity and Darwin corrections. Moreover, the corrections (as well as the sums of all the relativistic corrections) for neighboring vibrational states do not differ significantly. This effectively causes an additional cancellation. For the second transition, 2 → 1, the inclusion of the spin-spin and orbit-orbit corrections has a somewhat less significant effect than for the first transition, 1 → 0. Nonetheless, even for this transition it noticeably improves the agreement between the theoretical and experimental results.

This work has been supported by the National Science Foundation. We acknowledge the use of the SGI Altix 4700 supercomputer at the University of Arizona Center of Computing and Information Technology.

APPENDIX

In this appendix we consider the matrix elements of the orbit-orbit Hamiltonian (5) with explicitly correlated complex Gaussians (15). Everywhere below we will be using notations and conventions adopted from [5]. It is essential that the reader familiarizes himself/herself with that work prior to reading this appendix.

We will assume that the number of particles is N and after separating out the motion of the center of mass the number of degrees of freedom is $3n$, where $n=N-1$. If X is an $n\times n$ matrix then the expression $\mathbf{r}'X\mathbf{r}$ should be read as $\mathbf{r}'(X\otimes I_3)\mathbf{r}$. The ket in matrix elements is usually affected by a permutational symmetry transformation. Following [5], we will denote this by the tilde symbol:

$$|\tilde{\phi}_l\rangle = \exp(-\mathbf{r}'\tilde{C}_l\mathbf{r}) = \exp[-\mathbf{r}'(\tilde{A}_l + i\tilde{B}_l)\mathbf{r}]. \tag{A1}$$

Also, for convenience we will define:

$$\boldsymbol{\nabla}_i \equiv \boldsymbol{\nabla}_{\mathbf{r}_i},$$

$$A_{kl} = A_k + A_l, \quad \tilde{A}_{kl} = A_k + \tilde{A}_l,$$

$$B_{kl} = -B_k + B_l, \quad \tilde{B}_{kl} = -B_k + \tilde{B}_l,$$

$$\tilde{C}_{kl} = C_k^* + \tilde{C}_l = \tilde{A}_{kl} + i\tilde{B}_{kl}.$$

The asterisk in the last expression stands for complex conjugation. Since the matrix C_k is symmetric, its complex conjugate is equivalent to the Hermitian conjugate, $C_k^*=C_k^\dagger$. To keep expressions in matrix form whenever possible, we will be using the following $3n$-component vectors:

$$\mathbf{r} = \begin{bmatrix} \mathbf{r}_1 \\ \mathbf{r}_2 \\ \vdots \\ \mathbf{r}_n \end{bmatrix}, \quad \boldsymbol{\nabla}_{\mathbf{r}} = \begin{bmatrix} \boldsymbol{\nabla}_1 \\ \boldsymbol{\nabla}_2 \\ \vdots \\ \boldsymbol{\nabla}_n \end{bmatrix}. \tag{A2}$$

The expression for the overlap of two complex Gaussians is given by [5]

$$\langle \phi_k | \tilde{\phi}_l \rangle = \frac{\pi^{3n/2}}{|\tilde{C}_{kl}|^{3/2}}, \tag{A3}$$

where the vertical bars denote the determinant of a matrix. The Coulomb integral has the following forms [5]:

$$\left\langle \phi_k \left| \frac{1}{r_i} \right| \tilde{\phi}_l \right\rangle = \langle \phi_k | \tilde{\phi}_l \rangle \frac{2}{\sqrt{\pi}} \frac{1}{\mathrm{tr}(\tilde{C}_{kl}^{-1} J_{ii})^{1/2}}, \tag{A4}$$

$$\left\langle \phi_k \left| \frac{1}{r_{ij}} \right| \tilde{\phi}_l \right\rangle = \langle \phi_k | \tilde{\phi}_l \rangle \frac{2}{\sqrt{\pi}} \frac{1}{\mathrm{tr}(\tilde{C}_{kl}^{-1} J_{ij})^{1/2}}. \tag{A5}$$

In the formulas above, $\mathrm{tr}[\cdots]$ stands for the trace and $\tilde{C}_{kl}^{-1}$ is the inverse matrix. The matrix J_{ii} is defined as follows:

$$J_{ij} = \begin{cases} E_{ii} & \text{if } i=j, \\ E_{ii} + E_{jj} - E_{ij} - E_{ji} & \text{if } i \neq j, \end{cases} \tag{A6}$$

where E_{ij} is a matrix with 1 in the i,jth position and 0's elsewhere.

Let us first find two auxiliary integrals that will be needed further. If X is a symmetrix matrix, then

$$\begin{aligned} \left\langle \phi_k \left| \frac{1}{r_{ij}} (\mathbf{r}'X\mathbf{r}) \right| \tilde{\phi}_l \right\rangle &= -\frac{\partial}{\partial\alpha} \left\langle \phi_k \left| \frac{1}{r_{ij}} \exp[-\alpha\mathbf{r}'X\mathbf{r}] \right| \tilde{\phi}_l \right\rangle \Bigg|_{\alpha=0} \\ &= -\frac{\partial}{\partial\alpha} \frac{2\pi^{(3n-1)/2}}{|\tilde{C}_{kl} + \alpha X|^{3/2} \mathrm{tr}[(\tilde{C}_{kl} + \alpha X)^{-1} J_{ij}]^{1/2}} \Bigg|_{\alpha=0}, \end{aligned} \tag{A7}$$

which after differentiation gives

$$\left\langle \phi_k \left| \frac{1}{r_{ij}} (\mathbf{r}'X\mathbf{r}) \right| \tilde{\phi}_l \right\rangle = \left\langle \phi_k \left| \frac{1}{r_{ij}} \right| \tilde{\phi}_l \right\rangle \left(\frac{3}{2} \mathrm{tr}(\tilde{C}_{kl}^{-1} X) - \frac{1}{2} \frac{\mathrm{tr}(\tilde{C}_{kl}^{-1} X C_{kl}^{-1} J_{ij})}{\mathrm{tr}(C_{kl}^{-1} J_{ij})} \right). \tag{A8}$$

Above we used the fact that the derivative of the determinant is given by

$$\frac{\partial|X|}{\partial\alpha} = |X| \mathrm{tr}\left(X^{-1} \frac{\partial X}{\partial\alpha} \right). \tag{A9}$$

In the case when, instead of r_{ij} in (A8), we have r_i, J_{ij} needs be replaced by J_{ii}.

In a similar manner one obtains another integral (matrix Y is assumed to be symmetric, as well as X):

$$\begin{aligned} &\left\langle \phi_k \left| \frac{1}{r_{ij}} (\mathbf{r}'X\mathbf{r})(\mathbf{r}'Y\mathbf{r}) \right| \tilde{\phi}_l \right\rangle \\ &= \left\langle \phi_k \left| \frac{1}{r_{ij}} \right| \tilde{\phi}_l \right\rangle \Bigg[\frac{9}{4} \mathrm{tr}(\tilde{C}_{kl}^{-1} Y) \mathrm{tr}(\tilde{C}_{kl}^{-1} X) + \frac{3}{2} \mathrm{tr}(\tilde{C}_{kl}^{-1} Y \tilde{C}_{kl}^{-1} X) \\ &\quad - \frac{1}{\mathrm{tr}(C_{kl}^{-1} J_{ij})} \Bigg(\frac{3}{4} \mathrm{tr}(\tilde{C}_{kl}^{-1} Y) \mathrm{tr}(\tilde{C}_{kl}^{-1} X \tilde{C}_{kl}^{-1} J_{ij}) \\ &\quad + \frac{3}{4} \mathrm{tr}(\tilde{C}_{kl}^{-1} X) \mathrm{tr}(\tilde{C}_{kl}^{-1} Y \tilde{C}_{kl}^{-1} J_{ij}) + \frac{1}{2} \mathrm{tr}(\tilde{C}_{kl}^{-1} Y \tilde{C}_{kl}^{-1} X \tilde{C}_{kl}^{-1} J_{ij}) \\ &\quad + \frac{1}{2} \mathrm{tr}(\tilde{C}_{kl}^{-1} X \tilde{C}_{kl}^{-1} Y \tilde{C}_{kl}^{-1} J_{ij}) \Bigg) \\ &\quad + \frac{1}{\mathrm{tr}(C_{kl}^{-1} J_{ij})^2} \frac{3}{4} \mathrm{tr}(\tilde{C}_{kl}^{-1} Y \tilde{C}_{kl}^{-1} J_{ij}) \mathrm{tr}(\tilde{C}_{kl}^{-1} X \tilde{C}_{kl}^{-1} J_{ij}) \Bigg]. \end{aligned} \tag{A10}$$

The fact that X and Y are said to be symmetric does not narrow the generality. Each of these matrices represents some quadratic form and can always be made symmetric without changing the quadratic form itself. Thus, even if, for example, X does not happen to be symmetric we will assume that it is symmetrized by $X=(X+X')/2$ prior to evaluating the integrals.

In the matrix elements that we need to evaluate,

$$\langle \phi_k|\hat{H}_{\mathrm{OO}}|\tilde{\phi}_l\rangle = -\frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}\frac{q_0 q_j}{m_0 m_j}\left[\left\langle \phi_k\left|\frac{1}{r_j}\boldsymbol{\nabla}_i'\boldsymbol{\nabla}_j\right|\tilde{\phi}_l\right\rangle + \left\langle \phi_k\left|\frac{1}{r_j^3}\mathbf{r}_j'(\mathbf{r}_j'\boldsymbol{\nabla}_i)\boldsymbol{\nabla}_j\right|\tilde{\phi}_l\right\rangle\right] + \frac{1}{2}\sum_{i=1}^{n}\sum_{j>i}^{n}\frac{q_i q_j}{m_i m_j}\left[\left\langle \phi_k\left|\frac{1}{r_{ij}}\boldsymbol{\nabla}_i'\boldsymbol{\nabla}_j\right|\tilde{\phi}_l\right\rangle + \left\langle \phi_k\left|\frac{1}{r_{ij}^3}\mathbf{r}_{ij}'(\mathbf{r}_{ij}'\boldsymbol{\nabla}_i)\boldsymbol{\nabla}_j\right|\tilde{\phi}_l\right\rangle\right], \qquad \text{(A11)}$$

we can rewrite the operators in the matrix form:

$$\frac{1}{r_{ij}}\boldsymbol{\nabla}_i'\boldsymbol{\nabla}_j = \frac{1}{r_{ij}}\boldsymbol{\nabla}_{\mathbf{r}}'E_{ij}\boldsymbol{\nabla}_{\mathbf{r}}, \qquad \text{(A12)}$$

$$\frac{1}{r_j^3}\mathbf{r}_j'(\mathbf{r}_j'\boldsymbol{\nabla}_i)\boldsymbol{\nabla}_j = -\boldsymbol{\nabla}_{\mathbf{r}}'E_{jj}\frac{1}{r_j}(\mathbf{r}'E_{ji}\boldsymbol{\nabla}_{\mathbf{r}})\boldsymbol{\nabla}_{\mathbf{r}} + \frac{1}{r_j}\boldsymbol{\nabla}_{\mathbf{r}}'E_{jj}(\mathbf{r}'E_{ji}\boldsymbol{\nabla}_{\mathbf{r}})\boldsymbol{\nabla}_{\mathbf{r}}, \qquad \text{(A13)}$$

$$\frac{1}{r_{ij}^3}\mathbf{r}_{ij}'(\mathbf{r}_{ij}'\boldsymbol{\nabla}_i)\boldsymbol{\nabla}_j = -\boldsymbol{\nabla}_{\mathbf{r}}'E_{jj}\frac{1}{r_{ij}}[\mathbf{r}'(E_{ji}-E_{ii})\boldsymbol{\nabla}_{\mathbf{r}}]\boldsymbol{\nabla}_{\mathbf{r}} + \frac{1}{r_{ij}}\boldsymbol{\nabla}_{\mathbf{r}}'E_{jj}[\mathbf{r}'(E_{ji}-E_{ii})\boldsymbol{\nabla}_{\mathbf{r}}]\boldsymbol{\nabla}_{\mathbf{r}}. \qquad \text{(A14)}$$

With the following relation that holds true for an arbitrary matrix X:

$$(\boldsymbol{\nabla}_{\mathbf{r}}'X\boldsymbol{\nabla}_{\mathbf{r}})\tilde{\phi}_l = -6\,\mathrm{tr}(X\tilde{C}_l)\tilde{\phi}_l + 4(\mathbf{r}'\tilde{C}_lX'\tilde{C}_l\mathbf{r})\tilde{\phi}_l, \qquad \text{(A15)}$$

we can obtain the first and the third matrix elements of the right-hand side in (A11):

$$\left\langle \phi_k\left|\frac{1}{r_j}\boldsymbol{\nabla}_i'\boldsymbol{\nabla}_j\right|\tilde{\phi}_l\right\rangle = -6\,\mathrm{tr}(E_{ij}\tilde{C}_l)\left\langle \phi_k\left|\frac{1}{r_j}\right|\tilde{\phi}_l\right\rangle + 4\left\langle \phi_k\left|\frac{1}{r_j}(\mathbf{r}'\tilde{C}_lE_{ji}\tilde{C}_l\mathbf{r})\right|\tilde{\phi}_l\right\rangle, \qquad \text{(A16)}$$

$$\left\langle \phi_k\left|\frac{1}{r_{ij}}\boldsymbol{\nabla}_i'\boldsymbol{\nabla}_j\right|\tilde{\phi}_l\right\rangle = -6\,\mathrm{tr}(E_{ij}\tilde{C}_l)\left\langle \phi_k\left|\frac{1}{r_{ij}}\right|\tilde{\phi}_l\right\rangle + 4\left\langle \phi_k\left|\frac{1}{r_{ij}}(\mathbf{r}'\tilde{C}_lE_{ji}\tilde{C}_l\mathbf{r})\right|\tilde{\phi}_l\right\rangle. \qquad \text{(A17)}$$

The last terms in the two expressions above can be evaluated using formula (A8).

The second and the fourth matrix elements of the right-hand side in (A11) have the following forms:

$$\left\langle \phi_k\left|\frac{1}{r_j^3}\mathbf{r}_j'(\mathbf{r}_j'\boldsymbol{\nabla}_i)\boldsymbol{\nabla}_j\right|\tilde{\phi}_l\right\rangle = \left\langle \boldsymbol{\nabla}_{\mathbf{r}}\phi_k\left|\frac{1}{r_j}E_{jj}(\mathbf{r}'E_{ji}\boldsymbol{\nabla}_{\mathbf{r}})\right|\boldsymbol{\nabla}_{\mathbf{r}}\tilde{\phi}_l\right\rangle + \left\langle \phi_k\left|\frac{1}{r_j}\boldsymbol{\nabla}_{\mathbf{r}}'E_{jj}(\mathbf{r}'E_{ji}\boldsymbol{\nabla}_{\mathbf{r}})\right|\boldsymbol{\nabla}_{\mathbf{r}}\tilde{\phi}_l\right\rangle = 4\left\langle \phi_k\left|\frac{1}{r_j}\mathbf{r}'C_k^{\dagger}E_{jj}(\mathbf{r}'E_{ji}\boldsymbol{\nabla}_{\mathbf{r}})\tilde{C}_l\mathbf{r}\right|\tilde{\phi}_l\right\rangle - 2\left\langle \phi_k\left|\frac{1}{r_j}\boldsymbol{\nabla}_{\mathbf{r}}'E_{jj}(\mathbf{r}'E_{ji}\boldsymbol{\nabla}_{\mathbf{r}})\tilde{C}_l\mathbf{r}\right|\tilde{\phi}_l\right\rangle, \qquad \text{(A18)}$$

$$\left\langle \phi_k\left|\frac{1}{r_{ij}^3}\mathbf{r}_{ij}'(\mathbf{r}_{ij}'\boldsymbol{\nabla}_i)\boldsymbol{\nabla}_j\right|\tilde{\phi}_l\right\rangle = \left\langle \boldsymbol{\nabla}_{\mathbf{r}}\phi_k\left|\frac{1}{r_{ij}}E_{jj}[\mathbf{r}'(E_{ji}-E_{ii})\boldsymbol{\nabla}_{\mathbf{r}}]\right|\boldsymbol{\nabla}_{\mathbf{r}}\tilde{\phi}_l\right\rangle + \left\langle \phi_k\left|\frac{1}{r_{ij}}\boldsymbol{\nabla}_{\mathbf{r}}'E_{jj}[\mathbf{r}'(E_{ji}-E_{ii})\boldsymbol{\nabla}_{\mathbf{r}}]\right|\boldsymbol{\nabla}_{\mathbf{r}}\tilde{\phi}_l\right\rangle = 4\left\langle \phi_k\left|\frac{1}{r_{ij}}\mathbf{r}'C_k^{\dagger}E_{jj}[\mathbf{r}'(E_{ji}-E_{ii})\boldsymbol{\nabla}_{\mathbf{r}}]\tilde{C}_l\mathbf{r}\right|\tilde{\phi}_l\right\rangle - 2\left\langle \phi_k\left|\frac{1}{r_{ij}}\boldsymbol{\nabla}_{\mathbf{r}}'E_{jj}[\mathbf{r}'(E_{ji}-E_{ii})\boldsymbol{\nabla}_{\mathbf{r}}]\tilde{C}_l\mathbf{r}\right|\tilde{\phi}_l\right\rangle. \qquad \text{(A19)}$$

Here we used the fact that $\boldsymbol{\nabla}_{\mathbf{r}}\phi_k = -2C_k\mathbf{r}\phi_k$ and $\boldsymbol{\nabla}_{\mathbf{r}}\tilde{\phi}_l = -2\tilde{C}_l\mathbf{r}\tilde{\phi}_l$. By applying the following general formulas (where X and Y are assumed to be arbitrary matrices) to the right-hand sides of (A18) and (A19),

$$(\mathbf{r}'X\boldsymbol{\nabla}_{\mathbf{r}})\tilde{\phi}_l = -2(\mathbf{r}'X\tilde{C}_l\mathbf{r})\tilde{\phi}_l, \qquad \text{(A20)}$$

$$(\mathbf{r}'X\boldsymbol{\nabla}_{\mathbf{r}})Y\mathbf{r} = YX'\mathbf{r}, \qquad \text{(A21)}$$

$$(\mathbf{r}'Y\boldsymbol{\nabla}_{\mathbf{r}})(\mathbf{r}'X\mathbf{r}) = \mathbf{r}'Y(X+X')\mathbf{r}, \qquad \text{(A22)}$$

and using the commutation relation

$$\boldsymbol{\nabla}_{\mathbf{r}}'X\mathbf{r} = 3\,\mathrm{tr}(X) + \mathbf{r}'X'\boldsymbol{\nabla}_{\mathbf{r}}, \qquad \text{(A23)}$$

and after collecting similar terms we get

$$\left\langle \phi_k \left| \frac{1}{r_j^3}\mathbf{r}_j'(\mathbf{r}_j'\boldsymbol{\nabla}_i)\boldsymbol{\nabla}_j \right| \widetilde{\phi}_l \right\rangle = -6\mathrm{tr}(E_{ji}\widetilde{C}_l E_{jj})\left\langle \phi_k \left| \frac{1}{r_j} \right| \widetilde{\phi}_l \right\rangle + 4\left\langle \phi_k \left| \frac{1}{r_j}(\mathbf{r}' U\mathbf{r}) \right| \widetilde{\phi}_l \right\rangle - 8\left\langle \phi_k \left| \frac{1}{r_j}(\mathbf{r}'\widetilde{C}_{kl}E_{jj}\widetilde{C}_l\mathbf{r})(\mathbf{r}'E_{ji}\widetilde{C}_l\mathbf{r}) \right| \widetilde{\phi}_l \right\rangle, \tag{A24}$$

$$\left\langle \phi_k \left| \frac{1}{r_{ij}^3}\mathbf{r}_{ij}'(\mathbf{r}_{ij}'\boldsymbol{\nabla}_i)\boldsymbol{\nabla}_j \right| \widetilde{\phi}_l \right\rangle = -6\mathrm{tr}[(E_{ji}-E_{ii})\widetilde{C}_l E_{jj}]\left\langle \phi_k \left| \frac{1}{r_{ij}} \right| \widetilde{\phi}_l \right\rangle + 4\left\langle \phi_k \left| \frac{1}{r_{ij}}(\mathbf{r}' W\mathbf{r}) \right| \widetilde{\phi}_l \right\rangle - 8\left\langle \phi_k \left| \frac{1}{r_{ij}}(\mathbf{r}'\widetilde{C}_{kl}E_{jj}\widetilde{C}_l\mathbf{r})[\mathbf{r}'(E_{ji}-E_{ii})\widetilde{C}_l\mathbf{r}] \right| \widetilde{\phi}_l \right\rangle, \tag{A25}$$

where matrices U and W are given by

$$U = C_{kl}E_{jj}\widetilde{C}_l E_{ij} + E_{ji}\widetilde{C}_l E_{jj}\widetilde{C}_l + \widetilde{C}_l E_{jj}E_{ji}\widetilde{C}_l + 3\mathrm{tr}(\widetilde{C}_l E_{jj})E_{ji}\widetilde{C}_l, \tag{A26}$$

$$W = C_{kl}E_{jj}\widetilde{C}_l(E_{ij}-E_{ii}) + (E_{ji}-E_{ii})\widetilde{C}_l E_{jj}\widetilde{C}_l + \widetilde{C}_l E_{jj}(E_{ji}-E_{ii})\widetilde{C}_l + 3\mathrm{tr}(\widetilde{C}_l E_{jj})(E_{ji}-E_{ii})\widetilde{C}_l. \tag{A27}$$

The two last terms in expression (A24), as well as in expression (A25), can be evaluated using formulas (A8) and (A10).

It should be mentioned that the presented expressions for the matrix elements of the orbit-orbit Hamiltonian can be greatly simplified when implemented in a computer code, because such matrices as E_{ii}, E_{jj}, and J_{ii} are sparse and contain only one nonzero element.

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