Relativistic corrections to the non-Born-Oppenheimer energies of the lowest singlet Rydberg states of ³He and ⁴He

Monika Stanke
Department of Chemistry, University of Arizona, Tucson, Arizona 85721
and Institute of Physics, Nicholas Copernicus University, ul. Grudziadzka 5, PL 87-100 Toruń, Poland

Dariusz Kędziera
Department of Chemistry, Nicholas Copernicus University, ul. Gagarina 7, PL 87-100 Toruń, Poland

Sergiy Bubin
Department of Chemistry, University of Arizona, Tucson, Arizona 85721

Ludwik Adamowicz
Department of Chemistry, University of Arizona, Tucson, Arizona 85721
and Department of Physics, University of Arizona, Tucson, Arizona 85721

In this work the authors present an approach to calculate the leading-order relativistic corrections for ground and excited states of helium isotopomers. In the calculations they used variational wave functions expanded in terms of explicitly correlated Gaussians obtained without assuming the Born-Oppenheimer approximation. © 2007 American Institute of Physics.
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I. INTRODUCTION

The helium atom is a system that has been described in calculations since the very early stages of the development of quantum mechanics. It is also one of the systems where the experiment has achieved the highest levels of precision. Recent theoretical studies of the helium atom that include the works performed by Morton *et al.*,[1] Korobov and Yelkhovsky,[2] Korobov,[3] and Pachucki,[4–6] have demonstrated that by systematically including relativistic and QED corrections to the nonrelativistic energies of the ground and excited states of this system, one can achieve an accuracy of the predicted ionization and transition energies that in some cases exceed the accuracy of the present-day experiment. The recently published summary of the available theoretical and experimental results for bound stationary states of He by Morton *et al.*[1] demonstrates the high level agreement between theory and experiment very well. It also shows that for a few states such as $^21P_1$ and ^23P_J there is still some noticeable disagreement between the theory and the experiment.[6,7]

To achieve a high level of agreement between the experiment and the theory for electronic transition energies, the accounting for relativistic corrections that include, apart from the dominant α^2-dependent terms (where $\alpha=1/c$ is the fine structure constant), also QED terms[8] is needed. Including the latter terms made the QED part of the calculations for the He atom[1] essentially exact, up to terms of the order of α^3. Furthermore, terms of the order of α^4 were included for some lower states from the calculations performed by Korobov and Yelkhovsky,[2] by Yelkhovsky,[9] by Pachucki,[5] and by Drake and Martin.[10] Moreover, there are works where the QED terms of the order of α^6 for the He atom were calculated.[4,6]

The He calculations also included corrections for finite values of the ³He and ⁴He charge radii of 1.9659 and 1.167 fm, respectively, which were derived from the isotope shift measured by Shiner *et al.*[11] and from the measurements of the Lamb shift of the muonic hydrogen.[11,12] The theoretical results included in work Ref. 1 will be used as a reference for the results obtained in this work.

The aim of the present study is to describe the first stage of the development of a computational approach that has the capability of producing results for ground and excited states of atoms and, eventually, for molecular systems with more than two electrons with a similar accuracy as the results obtained for helium.[1] The most straightforward way of developing such an approach would be by extending the Slater-type or Hylleraas-type basis set used in the calculations reported in the work of Morton *et al.* to atomic systems with more than three electrons. However, such an extension has not been accomplished yet due to problems with calculating the necessary matrix elements with explicitly correlated Slater- or Hylleraas-type functions. Only calculations with three-electron integrals (or a total of four particles) have been reported thus far.[13–18] Alternative basis functions that can be used in very accurate atomic calculations are explicitly correlated Gaussian functions. Gaussians are less effective than Slaters in describing the cusp behavior of the wave functions, but their use leads to much easier integrals, which, for a one-center expansion of the wave function, can be analytically calculated using standard procedures for any number of electrons. In recent years we have used various types of Gaussian basis functions in very accurate atomic and molecular calculations. In those calculations we have employed an approach departing from the Born-Oppenheimer (BO) approximation, whose development has been carried out in our research group.[19–27] If the BO approximation is not assumed,

the motion of the electrons and the nuclei are treated on equal footing, and since these motions are highly correlated (coupled), one has to use basis functions that explicitly depend on the distances between the particles (nuclei and electrons) in expanding the wave function. The explicitly correlated Gaussians are such functions.

Recently, explicitly correlated Gaussians were used by Pachucki and Komasa[28,29] to calculate new variational upper bounds to the BO energies of the two lowest S states of the Be atom. They also calculated relativistic and QED energy corrections of the orders of α^2 and α^3 for those states. The corrections were determined as expectation values of the corresponding operators using the BO electronic wave functions. In addition they also calculated corrections due to the finite mass of the nucleus using the perturbation theory approach. Since the corrections are very small, the perturbative approach is capable of providing very accurate values of those corrections. There is an interesting analysis in the work of Pachucki *et al.*[30] concerning the accuracy of the relativistic integrals. They compare the direct algorithm of calculating those integrals with an algorithm based on the so-called "Drachmanization" and show that this procedure leads to a much faster convergence of the integral values with the size of the basis set. However, when the basis set size becomes large, the values obtained with the direct procedure and with the procedure based on the Drachmanization are virtually the same. Since in the present calculations we use very extended basis sets, the algorithms we developed are based on the direct approach.

The approach we have been developing is somewhat different from that of Pachucki and Komasa because in our nonrelativistic calculations we do not assume the BO approximation and the finite mass of the nucleus is explicitly included in generating the energy and the wave function. As a result, we obtain different wave functions and different energies for different isotopes. With those wave functions we then calculate expectation values of the relativistic operators. In this way our atomic relativistic corrections include not only the electronic contributions, but also contributions due to the nucleus. In this work we show the application of the approach in calculations of the α^2-dependent relativistic corrections to the energies of the ground and excited states of the S symmetry of ^{3}He and ^{4}He. These corrections include the mass-velocity and Darwin terms, as well as terms due to magnetic orbit-orbit and Fermi contact interactions. The algorithms for the former were derived for a more general case of a diatomic system in our recent works.[25–27] In the atomic case considered here, we used a simplified version of those algorithms. The algorithms for the latter terms have been derived and implemented in this work.

The calculations of the relativistic effects using the non-BO wave functions allow for a direct calculation of the isotopic energy shifts of such quantities as the ionization potential and transition energies. In this work we show calculations of those shifts for the ^{3}He and ^{4}He isotopes.

II. THE METHOD USED IN THE CALCULATIONS

A. The internal Hamiltonian

The total nonrelativistic Hamiltonian can be exactly separated into the Hamiltonian representing the kinetic energy of the center-of-mass motion and the internal Hamiltonian. In our approach, this transformation is done by replacing the laboratory coordinate system by a new system whose first three coordinates are the laboratory Cartesian coordinates of the center of mass, $\mathbf{r}_0$, and the remaining coordinates are internal Cartesian coordinates. The origin of the internal coordinate system is placed at the nucleus (particle 1 with mass M_1 called the reference particle). The other particles (electrons) are referred to as the reference particle using the Cartesian position vectors $\mathbf{r}_i$. The internal Hamiltonian H_{int} for the helium atom is

$$H_{\text{int}} = -\frac{1}{2}\left(\sum_{i=1}^{2} \frac{1}{\mu_i} \nabla_{\mathbf{r}_i}^2 + \sum_{i=1}^{2}\sum_{j\neq i}^{2} \frac{1}{M_1} \nabla_{\mathbf{r}_i} \cdot \nabla_{\mathbf{r}_j} \right)$$
$$+ \sum_{i=1}^{2} \frac{q_0 q_i}{r_i} + \sum_{i=1}^{2}\sum_{i<j}^{2} \frac{q_i q_j}{r_{ij}}. \tag{1}$$

The internal Hamiltonian [Eq. (1)] describes two pseudoparticles (pseudoelectrons) with charges $q_i = -1$, $i = 1, 2$, and reduced masses $\mu_i = M_1 M_{i+1}/(M_1 + M_{i+1})$ (where $M_2 = M_3 = 1$ are electron masses) moving in the central potential of the charge of the reference particle ($q_0 = 2$). The motions of the pseudoparticles are coupled through the mass polarization term $\sum_{i=1}^{2}\sum_{j\neq i}^{2} 1/M_1 \nabla_{\mathbf{r}_i} \cdot \nabla_{\mathbf{r}_j}$ and through the Coulombic interactions dependent on the distances of the pseudoparticles from the central charge, $r_i = |\mathbf{r}_i|$, and their relative distances, $r_{ij} = |\mathbf{r}_j - \mathbf{r}_i|$.

B. Relativistic Hamiltonian for many-particle systems

For small atomic and molecular systems the account of the relativistic and QED effects is usually done using the first-order perturbation theory and calculating those corrections as expectation values of the corresponding operators. The corrections can be grouped into terms, each proportional to a certain power of the fine structure constant α,

$$H = H_{\text{int}} + \alpha^2 H_{\text{rel}} + \alpha^3 H_{\text{QED}(3)} + \alpha^4 H_{\text{QED}(4)} + \cdots,$$

where H_{int} is the nonrelativistic Hamiltonian described in the previous section, H_{rel} includes all relativistic terms whose contributions are proportional to α^2, and $H_{\text{QED}(3)}$ and $H_{\text{QED}(4)}$ group all contributions proportional to α^3, α^4, etc. We will now discuss the α^2 contributions in the case of the He atom, where either all particles are fermions and have spins equal to $1/2$ (the ^{3}He case), or where two particles have spins equal to $1/2$ and the third is a boson (α-particle) with a zero spin (the ^{4}He case).

While a full separation of the laboratory Hamiltonian into the Hamiltonian describing the kinetic energy of the center-of-mass motion and the internal Hamiltonian can be exactly performed, the separation of the relativistic Hamiltonian into the internal and external parts is not exact. In general, the Breit-Pauli Hamiltonian after the transforma-

tion from the laboratory coordinate system to the new system of coordinates can be written as a sum of three terms,

$$H_{rel} = H_{rel}^{CM} + H_{rel}^{int} + H_{rel}^{CM\text{-}int},$$

where H_{rel}^{CM} is the term describing the relativistic effects of the motion of the center of mass, H_{rel}^{int} describes the internal relativistic effects, and $H_{rel}^{CM\text{-}int}$ describes the relativistic coupling of the internal and external motions. The relativistic corrections to the internal states of the system are calculated using H_{rel}^{int}. For states with the S symmetry of ^{4}He and ^{3}He, the transformation of the coordinate system leads to the internal relativistic operators in the following form:

$$H_{rel}^{int}(^4\mathrm{He}) = -\frac{1}{8}\left[\frac{1}{m_0^3}(\nabla_1+\nabla_2)^4 + \frac{1}{m_1^3}\nabla_1^4 + \frac{1}{m_2^3}\nabla_2^4\right] - \frac{\pi}{2}\left[\frac{1}{m_1^2}q_0q_1\delta^3(r_1) + \frac{1}{m_2^2}q_0q_2\delta^3(r_2) + \left(\frac{1}{m_1^2}+\frac{1}{m_2^2}\right)q_2q_1\delta^3(\mathbf{r}_{12})\right]$$

$$-\frac{1}{2}\frac{q_0q_1}{m_0m_1}\left[\frac{1}{r_1}\nabla_1\cdot\nabla_1 + \frac{1}{r_1^3}\mathbf{r}_1\cdot(\mathbf{r}_1\cdot\nabla_1)\nabla_1\right] - \frac{1}{2}\frac{q_0q_2}{m_0m_2}\left[\frac{1}{r_2}\nabla_2\cdot\nabla_2 + \frac{1}{r_2^3}\mathbf{r}_2\cdot(\mathbf{r}_2\cdot\nabla_2)\nabla_2\right] - \frac{1}{2}\frac{q_0q_1}{m_0m_1}\left[\frac{1}{r_1}\nabla_1\cdot\nabla_2\right.$$

$$\left.+\frac{1}{r_1^3}\mathbf{r}_1\cdot(\mathbf{r}_1\cdot\nabla_1)\nabla_2\right] - \frac{1}{2}\frac{q_0q_2}{m_0m_2}\left[\frac{1}{r_2}\nabla_2\cdot\nabla_1 + \frac{1}{r_2^3}\mathbf{r}_2\cdot(\mathbf{r}_2\cdot\nabla_2)\nabla_1\right] + \frac{1}{2}\frac{q_1q_2}{m_1m_2}\left[\frac{1}{r_{12}}\nabla_1\cdot\nabla_2 + \frac{1}{r_{12}^3}\mathbf{r}_{12}\cdot(\mathbf{r}_{12}\cdot\nabla_1)\nabla_2\right]$$

$$-\frac{8\pi}{3}[(\mathbf{S}_1\cdot\mathbf{S}_2)\delta^3(\mathbf{r}_{12})]$$

and

$$H_{rel}^{int}(^3\mathrm{He}) = H_{rel}^{int}(^4\mathrm{He}) + \frac{\pi}{2}\left[\frac{1}{m_0^2}q_0q_1\delta^3(\mathbf{r}_1) + \frac{1}{m_0^2}q_0q_2\delta^3(\mathbf{r}_2)\right] - \frac{8\pi}{3}\left[\frac{q_0q_1}{m_0m_1}(\mathbf{S}_0\cdot\mathbf{S}_1)\delta^3(\mathbf{r}_1) + \frac{q_0q_2}{m_0m_2}(\mathbf{S}_0\cdot\mathbf{S}_2)\delta^3(\mathbf{r}_2)\right]. \qquad (2)$$

The difference between the two Hamiltonians $H_{rel}^{int}(^4\mathrm{He})$ and $H_{rel}^{int}(^3\mathrm{He})$ results from the fact the ^{3}He nucleus is a fermion with spin $\frac{1}{2}$ and the ^{4}He nucleus is a boson with zero spin.

III. RESULTS

The general form of the basis function used here to calculate states of the S symmetry for ^{3}He and ^{4}He is ($\otimes$ is the Kronecker product symbol),

$$\phi_k = \exp[-\mathbf{r}'(L_k L_k' \otimes I_3)\mathbf{r}], \qquad (3)$$

where for He, the $\mathbf{r}$ vector is a six-component vector of the internal Cartesian coordinates of the two pseudoparticles, L_k is a 2×2 rank 2 lower triangular matrix of nonlinear variation parameters, and I_3 is the 3×3 identity matrix. To ensure the proper permutational symmetry of the two electrons, the appropriate symmetry projections were applied to the basis functions. The wave functions for the ground state and the excited states were obtained using the variational method by minimizing the energy of each state in a separate calculation. The minimization was done with respect to the linear expansion coefficients c_k and with respect to the nonlinear parameters of the basis functions, i.e., the basis set exponent matrices L_k. In the minimization we used analytically calculated gradients of the energy with respect to $\{c_k\}$ and $\{L_k\}$. The use of the analytical gradient was key in obtaining very accurate results in the energy minimization.

1500 Gaussians for each state were used in our calculations. Our previous experience with atomic calculations have shown that it is not necessary to optimize the linear

parameters for all the isotopes. Equally accurate results can be obtained by performing nonlinear parameter optimization and generating the basis set for one of the isotopes (^{4}He is this work) and using it in the calculations of other isotopes where only the linear parameters are optimized through the diagonalization of the Hamiltonian matrix. Such an approach has been employed in this work. Apart from ^{3}He and ^{4}He calculations, we also performed calculations for $^\infty$He which are equivalent to calculations where the Born-Oppenheimer approximation is assumed.

After the wave functions were generated, expectation values of the internal relativistic operator have been calculated. The algorithms for the mass-velocity and Darwin terms have been derived and implemented in our previous works.[25–27] In this work we have derived and implemented the algorithms for calculating the orbit-orbit and spin-spin interactions. A detailed description of the algorithms will be presented elsewhere.[31] One way those algorithms were tested was based on the Hermiticity of the orbit-orbit operator. Since this property is not as straightforward as for other relativistic operators, we included a short discussion on this point in the Appendix.

The results of the calculations that include all relativistic corrections of the order of α^2 and the nonrelativistic and relativistic total energies are shown in Table I for ^{3}He, ^{4}He, and $^\infty$He. The results for the ^{4}He ground state can be directly compared with the values obtained by Korobov and Yelkhovsky.[2] Their ground state energy obtained with the nucleus-to-electron mass ratio of 7294.299 508(16)

TABLE I. Nonrelativistic and relativistic total energies of six lowest S states of the helium atom and the leading relativistic α^2-dependent corrections: mass-velocity (E_{MV}), Darwin (E_D), spin-spin (E_{SS}), orbit-orbit (E_{OO}). $E_{\text{tot.corr.}}$ is the sum of all corrections. All numbers are in a.u.

State	Isotop	E_{nonrel}	E_{MV}	E_D	E_{SS}	E_{OO}	$E_{\text{tot.corr.}}$	E_{rel}
1S	^{3}He	−2.903 167 210 710	$-7.195\,249\,97\times10^{-4}$	$5.876\,243\,14\times10^{-4}$	$3.556\,476\,69\times10^{-5}$	$-7.616\,067\,78\times10^{-6}$	$-1.039\,519\,84\times10^{-4}$	−2.903 271 162 695
	^{4}He	−2.903 304 557 729	$-7.196\,566\,87\times10^{-4}$	$5.877\,046\,44\times10^{-4}$	$3.556\,973\,76\times10^{-5}$	$-7.564\,540\,48\times10^{-6}$	$-1.039\,468\,45\times10^{-4}$	−2.903 408 504 575
	$^\infty$He	−2.903 724 377 034	$-7.200\,593\,20\times10^{-4}$	$5.879\,502\,88\times10^{-4}$	$3.558\,493\,39\times10^{-5}$	$-7.406\,980\,79\times10^{-6}$	$-1.039\,310\,79\times10^{-4}$	−2.903 828 808 113
2S	^{3}He	−2.145 581 923 701	$-5.469\,997\,21\times10^{-4}$	$4.364\,368\,53\times10^{-4}$	$2.892\,914\,21\times10^{-6}$	$-6.523\,944\,03\times10^{-7}$	$-1.083\,223\,49\times10^{-4}$	−2.145 690 246 049
	^{4}He	−2.145 678 587 578	$-5.470\,980\,12\times10^{-4}$	$4.364\,955\,89\times10^{-4}$	$2.893\,276\,91\times10^{-6}$	$-6.130\,474\,06\times10^{-7}$	$-1.083\,221\,94\times10^{-4}$	−2.145 786 909 772
	$^\infty$He	−2.145 974 046 052	$-5.473\,985\,24\times10^{-4}$	$4.366\,751\,95\times10^{-4}$	$2.894\,385\,85\times10^{-6}$	$-4.927\,373\,45\times10^{-7}$	$-1.083\,216\,81\times10^{-4}$	−2.146 082 367 733
3S	^{3}He	−2.060 896 524 119	$-5.363\,311\,21\times10^{-4}$	$4.286\,693\,62\times10^{-4}$	$8.139\,081\,51\times10^{-7}$	$-2.931\,082\,42\times10^{-7}$	$-1.071\,409\,60\times10^{-4}$	−2.061 003 665 079
	^{4}He	−2.060 989 082 344	$-5.364\,273\,90\times10^{-4}$	$4.287\,270\,34\times10^{-4}$	$8.140\,086\,24\times10^{-7}$	$-2.545\,870\,12\times10^{-7}$	$-1.071\,409\,34\times10^{-4}$	−2.061 096 223 278
	$^\infty$He	−2.061 271 989 736	$-5.367\,217\,18\times10^{-4}$	$4.289\,033\,87\times10^{-4}$	$8.143\,158\,14\times10^{-7}$	$-1.368\,027\,59\times10^{-7}$	$-1.071\,408\,18\times10^{-4}$	−2.061 379 130 554
4S	^{3}He	−2.033 216 570 271	$-5.338\,524\,55\times10^{-4}$	$4.269\,394\,58\times10^{-4}$	$3.340\,110\,39\times10^{-7}$	$-2.113\,388\,35\times10^{-7}$	$-1.067\,903\,24\times10^{-4}$	−2.033 323 360 595
	^{4}He	−2.033 307 817 477	$-5.339\,482\,56\times10^{-4}$	$4.269\,968\,96\times10^{-4}$	$3.340\,519\,70\times10^{-7}$	$-1.730\,130\,04\times10^{-7}$	$-1.067\,903\,22\times10^{-4}$	−2.033 414 607 799
	$^\infty$He	−2.033 586 717 026	$-5.342\,411\,56\times10^{-4}$	$4.271\,725\,31\times10^{-4}$	$3.341\,771\,16\times10^{-7}$	$-5.582\,648\,36\times10^{-8}$	$-1.067\,902\,75\times10^{-4}$	−2.033 693 507 301
5S	^{3}He	−2.020 809 059 294	$-5.329\,909\,03\times10^{-4}$	$4.263\,506\,46\times10^{-4}$	$1.680\,275\,50\times10^{-7}$	$-1.832\,459\,63\times10^{-7}$	$-1.066\,554\,75\times10^{-4}$	−2.020 915 714 770
	^{4}He	−2.020 899 726 154	$-5.330\,865\,43\times10^{-4}$	$4.264\,080\,04\times10^{-4}$	$1.680\,480\,51\times10^{-7}$	$-1.449\,888\,70\times10^{-7}$	$-1.066\,554\,79\times10^{-4}$	−2.021 006 381 633
	$^\infty$He	−2.021 176 851 555	$-5.333\,789\,48\times10^{-4}$	$4.265\,833\,97\times10^{-4}$	$1.681\,107\,33\times10^{-7}$	$-2.801\,263\,81\times10^{-8}$	$-1.066\,554\,53\times10^{-4}$	−2.021 283 507 007
6S	^{3}He	−2.014 196 551 188	$-5.326\,187\,04\times10^{-4}$	$4.260\,989\,59\times10^{-4}$	$9.610\,479\,87\times10^{-8}$	$-1.711\,041\,94\times10^{-7}$	$-1.065\,947\,44\times10^{-4}$	−2.014 303 145 932
	^{4}He	−2.014 286 911 171	$-5.327\,142\,77\times10^{-4}$	$4.261\,562\,86\times10^{-4}$	$9.611\,649\,58\times10^{-8}$	$-1.328\,772\,61\times10^{-7}$	$-1.065\,947\,52\times10^{-4}$	−2.014 393 505 923
	$^\infty$He	−2.014 563 098 433	$-5.330\,064\,79\times10^{-4}$	$4.263\,315\,80\times10^{-4}$	$9.615\,225\,89\times10^{-8}$	$-1.599\,330\,99\times10^{-8}$	$-1.065\,947\,39\times10^{-4}$	−2.014 669 693 173

TABLE II. Nonrelativistic transition energies in comparison with relativistically corrected ones. All numbers are in megahertz.

Transition	Isotope	ΔE_{nonrel}	ΔE_{rel}	Morton *et al.* (Ref. [1])	Expt. (Ref. [1])
$2S \rightarrow 1S$	^{3}He	498 467 173 2	498 464 297 6	498 460 453 0	498 460 459 3
	^{4}He	498 493 941 4	498 491 062 5	498 487 218 6	498 487 219 1
	$^\infty$He	498 575 766 9	498 572 878 0		
$3S \rightarrow 2S$	^{3}He	557 203 162	557 210 935	557 208 896	
	^{4}He	557 230 176	557 237 948	557 235 909	557 235 927
	$^\infty$He	557 312 758	557 320 528		
$4S \rightarrow 3S$	^{3}He	182 125 347	182 127 654	182 127 194	
	^{4}He	182 133 973	182 136 280	182 135 821	
	$^\infty$He	182 160 344	182 162 650		
$5S \rightarrow 4S$	^{3}He	816 375 00	816 383 88	816 382 34	
	^{4}He	816 413 19	816 422 06	816 420 53	
	$^\infty$He	816 529 92	816 538 79		
$6S \rightarrow 5S$	^{3}He	435 082 13	435 086 13	435 085 57	
	^{4}He	435 102 32	435 106 32	435 105 76	
	$^\infty$He	435 164 05	435 168 05		

$$E = -2.903\ 304\ 557\ 727\ 940\ 23(1) \text{ a.u.}$$

is slightly higher than ours,

$$E = -2.903\ 304\ 557\ 729 \text{ a.u.}$$

Since we only used the double precision in the calculations, the number of significant figures reported in the energy is smaller than the number of significant figures in the results of Korobov and Yelkhovsky. In our calculations we used more current values of the physical constants and masses taken from CODATA 2002 Ref. [32] with the ^{3}He and ^{4}He nuclear masses equal to 5495.885 269 and 7294.299 536 3, respectively. Since our ^{4}He nuclear mass is slightly larger than that used by Korobov and Yelkhovsky, we recalculated the ^{4}He ground state energy using our basis set and their mass, and we obtained the value

$$E = -2.903\ 304\ 557\ 727\ 57 \text{ a.u.},$$

which is slightly higher than their energy. A comparison can also be made between the relativistic correction of the order of α^2 of Korobov and Yelkhovsky. They reported a value of $-1.952\ 050\ 77(1)\alpha^2$,[2] while our value is $-1.952\ 003\ 57\alpha^2$.

Upon examining the results shown in Table I, one can notice that the mass-velocity, Darwin, and spin-spin relativistic corrections increase slightly in magnitude with the increase of the nuclear mass for all six S Rydberg states calculated here. The increased mass of the nucleus leads to a slight spatial contraction of the system, higher average velocity of the electrons, and higher values of the electron-electron and electron-nucleus contact terms. This explains the increase of the mass-velocity, Darwin, and spin-spin relativistic corrections. This increasing trend is, however, not followed by the orbit-orbit correction. Here, not only does the correction decreases in magnitude with the rising mass of the nucleus, but this decrease also significantly accelerates for higher states. In those higher states, one of the electrons becomes excited to states that are increasingly more diffuse. When this hap-

pens, the average distance of the excited electron from the nucleus significantly increases, and the radius of the motion of the nucleus around the center of mass of the system also increases. This effect is sensitive to the mass of the nuclei. For the infinite mass the radius of the motion of the nucleus around the center of mass becomes zero. This may explain the large difference between the orbit-orbit contribution for finite and infinite nuclear masses of the nucleus in higher Rydberg states.

Next, we used the calculated nonrelativistic and relativistic total energies of ^{3}He, ^{4}He, and $^\infty$He to determine the transition energies between the consecutive states. The transition energies are presented in Table II along with a comparison with the available experimental and calculated values obtained form ionization energies taken from the work of Morton *et al.*[1] As mentioned before, those previously calculated values also include relativistic and QED corrections of higher orders in α, and, due to that, are more accurate than our values.

IV. SUMMARY

In this work we have shown that the gradient based variational optimization of explicitly correlated Gaussian functions leads to energies of ground and excited energies of the He atom, which agree very well with the best previously obtained values. The Gaussians seem to be capable of very well describing the oscillatory nature of the wave function which increases with the level of excitation. Unlike most of the previous atomic calculations, in the present approach we have not assumed the Born-Oppenheimer approximation regarding the separability of the electronic and nuclear motions. Thus, slightly different wave functions have been obtained for different He isotopomers. These functions have been used to calculate isotope-dependent relativistic corrections of the order of α^2.

Our future work will include extending the approach presented in this work to diatomic molecules and to states with a rotational quantum number higher than zero. Diatomic calculations will require the use of basis functions where the Gaussian exponents [Eq. (3)] are multiplied by powers of the internuclear distance.

APPENDIX: HERMITICITY OF THE ORBIT-ORBIT OPERATOR

In the laboratory Cartesian coordinate frame the orbit-orbit operator has the following form:

$$H_{OO} = \frac{1}{2}\sum_{i=1}^{N}\sum_{j>i}^{N}\frac{Q_i Q_j}{M_i M_j}\left[\frac{1}{R_{ij}}\nabla_i \cdot \nabla_j + \frac{1}{R_{ij}^3}\mathbf{R}_{ij}\cdot(\mathbf{R}_{ij}\cdot\nabla_i)\nabla_j\right].$$

To simplify the problem let us consider a two-electron system where the orbit-orbit Hamiltonian is

$$H_{OO} = \frac{1}{2}\frac{e^2}{m_e^2}\left[\frac{1}{r_{12}}\nabla_1 \cdot \nabla_2 + \frac{1}{r_{12}^3}\mathbf{r}_{12}\cdot(\mathbf{r}_{12}\cdot\nabla_1)\nabla_2\right].$$

We will show that the Hermiticity of H_{OO} is a result of the cancellation of certain contributions resulting from the first part of the operator, $H_1 \propto 1/r_{12}\nabla_1\cdot\nabla_2$, and contributions resulting from its second part, $H_2 \propto 1/r_{12}^3\mathbf{r}_{12}\cdot(\mathbf{r}_{12}\cdot\nabla_1)\nabla_2$. We should note that H_1 and H_2 are not Hermitian by themselves. The Hermiticity of H_{OO} can be shown using the following commutational relations:

$$\left[\nabla_2,\frac{1}{r_{12}}\right] = -\left[\nabla_1,\frac{1}{r_{12}}\right] = \frac{\mathbf{r}_{12}}{r_{12}^3},$$

$$\left[\nabla_2,\frac{\mathbf{r}_{12}}{r_{12}^3}\right] = -\left[\nabla_1,\frac{\mathbf{r}_{12}}{r_{12}^3}\right] = -4\pi\delta^3(r_{12}),$$

$$[\nabla_2,\mathbf{r}_{12}] = -[\nabla_1,\mathbf{r}_{12}] = -3,$$

$$[\mathbf{A}\nabla_2,\mathbf{r}_{12}] = -[\mathbf{A}\nabla_1,\mathbf{r}_{12}] = -\mathbf{A},$$

where $\mathbf{A}$ is an arbitrary vector operator. Applying the above commutational relations to H_1 and H_2, we get

$$\left[\nabla_1\cdot\nabla_2,\frac{1}{r_{12}}\right] = \frac{\mathbf{r}_{12}}{r_{12}^3}\nabla_1 - \frac{\mathbf{r}_{12}}{r_{12}^3}\nabla_2 + 4\pi\delta^3(r_{12}), \quad (A1)$$

$$\left[\nabla_1\cdot\nabla_2,\frac{\mathbf{r}_{12}}{r_{12}^3}\mathbf{r}_{12}\right] = -\frac{\mathbf{r}_{12}}{r_{12}^3}\nabla_1 + \frac{\mathbf{r}_{12}}{r_{12}^3}\nabla_2 - 4\pi\delta^3(r_{12}) + a, \quad (A2)$$

where a is an operator whose expectation value is zero. Now, we add the two equations, [Eqs. (A1) and (A2)], and we get

the following expression for the expectation value of the orbit-orbit interaction operator:

$$\left\langle\frac{1}{r_{12}}\nabla_1\cdot\nabla_2\right\rangle + \left\langle\frac{\mathbf{r}_{12}}{r_{12}^3}\cdot(\mathbf{r}_{12}\cdot\nabla_1)\nabla_2\right\rangle$$

$$= \left\langle\nabla_1\cdot\nabla_2\frac{1}{r_{12}}\right\rangle + \left\langle\frac{\mathbf{r}_{12}}{r_{12}^3}\cdot\nabla_2\right\rangle - \left\langle\frac{\mathbf{r}_{12}}{r_{12}^3}\cdot\nabla_1\right\rangle$$

$$- 4\pi\langle\delta^3(r_{12})\rangle + \left\langle\nabla_1\cdot\left(\nabla_2\cdot\frac{\mathbf{r}_{12}}{r_{12}^3}\right)\mathbf{r}_{12}\right\rangle$$

$$- \left\langle\frac{\mathbf{r}_{12}}{r_{12}^3}\cdot\nabla_1\right\rangle + 4\pi\langle\delta^3(r_{12})\rangle$$

$$= \left\langle\nabla_1\cdot\nabla_2\frac{1}{r_{12}}\right\rangle + \left\langle\nabla_1\cdot\left(\nabla_2\cdot\frac{\mathbf{r}_{12}}{r_{12}^3}\right)\mathbf{r}_{12}\right\rangle,$$

which clearly shows its Hermiticity.

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