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Calculation of the Positron Annihilation Rate in PsH with the Positronic Extension of the Explicitly Correlated Nuclear−Electronic Orbital Method[†]

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The nuclear−electronic orbital explicitly correlated Hartree−Fock (NEO-XCHF) method is modified and extended to study electron−positron quantum systems. The NEO-XCHF method is more computationally efficient than the explicitly correlated methods previously applied to positron systems because only the electron−positron dynamical correlation is treated explicitly in NEO-XCHF. As a result, the form of the wave function is much simpler with fewer parameters, and the variational optimization of the molecular orbital parameters is performed through an iterative scheme rather than a stochastic optimization. The NEO-XCHF approach is used to calculate the positron annihilation rate for positronium hydride (PsH). The resulting annihilation rate for PsH is within 20% of the most accurate values available and is calculated at a fraction of the computational cost. These results suggest that qualitatively accurate positron annihilation rates can be calculated treating only electron−positron correlation explicitly, leading to significant computational savings by neglecting electron−electron dynamical correlation. Thus, the NEO-XCHF approach could potentially enable the calculation of qualitatively accurate positron annihilation rates for larger positron systems.

I. Introduction

The theory of bound positrons has multiple applications in diverse fields such as chemistry, solid state physics, and astrophysics.[1−4] In medical fields, positron emission tomography has been shown to be a useful technique for molecular imaging of biological processes with high diagnostic accuracy.[5,6] These wide-ranging applications will continue to grow as new high-intensity sources and better detection techniques are developed. The main observable that a successful theory of bound positrons should be able to predict is the positron annihilation rate, a highly local property that depends very strongly on the accuracy of the electronic−positronic wave function in the region of small electron−positron distances. The experimentally measured positron annihilation rates for molecular systems vary widely, and the interpretation of the experimental data has been debated in the literature.[7,8]

Although high-level theoretical calculations have been performed for small positronic systems,[9−24] such as positronium hydride (PsH) and e^+−LiH, theoretical studies of larger positronic systems are limited. A major computational challenge for studying positronic systems is accounting for the significant electron−positron correlation. In contrast to purely electronic systems, the electron−positron attractive Coulomb interaction leads to large probability densities at small electron−positron distances. As a result, dynamical correlation plays a considerably more important role for mixed electron−positron systems than for purely electronic systems. Another computational challenge arises from the importance of three-body interactions in mixed electron−positron systems. Since the Pauli principle does not prevent three-body collisions when both electrons and positrons are involved, the three-body effects must be adequately treated in these types of systems.[25]

Previous calculations indicate that conventional electronic structure methods for treating dynamical correlation are not adequate for mixed electron−positron systems. For example, recently the nuclear−electronic orbital (NEO) method[26] was modified and extended to positron systems.[27] In this approach, all electrons and the positron are treated quantum mechanically with molecular orbital techniques, while the nuclei are represented as classical point charges. For convenience, the notation “NEO” is retained for this positronic extension. For PsH, a NEO-HF (Hartree−Fock) calculation with a reasonably large basis set produced an annihilation rate that is almost an order of magnitude smaller than the most accurate results for this system, while a perturbative treatment of dynamical electron−positron correlation with the NEO-MP2 (second-order perturbation theory) approach led to only a small improvement.[27] A NEO-FCI (full configuration interaction) treatment with a tractable basis set produced an annihilation rate that is still less than 50% of the most accurate results for this system.[27] The FCI convergence for the same system was previously investigated by Mitroy and co-workers,[22] who also identified difficulties with convergence of traditional CI approaches for electron−positron systems.

Successful calculations of positron annihilation rates in small systems such as PsH have relied on an explicit treatment of dynamical correlation. Typically the wave function is chosen to have an analytical form that is capable of reproducing the behavior of the exact wave function in all regions of coordinate space, including very small interparticle distances. For example, the explicitly correlated wave functions used in ref 21 and ref 24 are capable of describing the cusp properties with high accuracy. In these types of studies, the parameters of the wave function are optimized variationally. The most accurate calculations involve stochastic variational optimization of at least hundreds of parameters defining the explicitly correlated wave functions. While these calculations typically produce highly accurate annihilation rates in excellent agreement with each

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other,[21,24] they are computationally expensive and are not easily extended to systems with more than a few electrons.

One common feature of these previous explicitly correlated approaches is that they treat the electron−electron and electron−positron correlation on the same level. As mentioned above, however, electron−positron dynamical correlation is much more significant than electron−electron dynamical correlation because of the attractive electron−positron Coulomb interaction. Moreover, the positron annihilation rate depends mainly on the electronic−positronic wave function in the region of small electron−positron distances and hence is more dependent upon an accurate treatment of electron−positron dynamical correlation than electron−electron dynamical correlation. Thus, we expect that qualitatively accurate positron: annihilation rates could be calculated with a method that treats only electron−positron correlation explicitly in the wave function. Given the nature of positronic systems, which usually include only a single positron, this simplification would result in significant computational savings.

In this paper, we use the NEO-XCHF (explicitly correlated Hartree−Fock) method[28,29] to test this hypothesis by calculating the positron annihilation rate for PsH. The NEO-XCHF method, which was previously developed for including dynamical electron−proton correlation in systems where selected hydrogen nuclei are treated quantum mechanically on the same level as the electrons,[28,29] is easily modified to study electron−positron quantum systems. One important difference between the NEO-XCHF approach and the explicitly correlated approaches previously applied to positron systems is that only the electron−positron correlation is treated explicitly in NEO-XCHF. As a result, the form of the wave function is much simpler with fewer parameters, and the variational optimization of the molecular orbital parameters is performed through an iterative scheme rather than a stochastic optimization. This approach is not expected to be more accurate than many other methods that were used successfully to calculate positron annihilation rates in small positron systems, but it is designed to be more easily extendable to larger systems. Our objective is to develop a qualitatively accurate method for calculating positron annihilation rates that can be extended to larger systems of biomedical and technological interest.

An outline of this paper is as follows. In section II, we present the extension of the NEO-XCHF method to positron systems and the expression used to calculate the positron annihilation rate. In section III, we describe the application of the NEO-XCHF method to PsH, which consists of a proton, two electrons, and a positron. PsH is an ideal system for benchmarking purposes because highly accurate energies and annihilation rates have been calculated with a variety of methods. Conclusions are presented in section IV.

II. Theory

The Hamiltonian for a system with one positron, N_e electrons, and N_c classical nuclei is

$$\hat{H} = -\frac{1}{2}\sum_{i}^{N_e}\nabla_i^2 - \sum_{i}^{N_e}\sum_{A}^{N_c}\frac{Z_A}{|\mathbf{r}_i^e - \mathbf{r}_A^c|} + \frac{1}{2}\sum_{i\neq j}^{N_e}\frac{1}{|\mathbf{r}_i^e - \mathbf{r}_j^e|} - \frac{1}{2}\nabla_p^2 + \sum_{A}^{N_c}\frac{Z_A}{|\mathbf{r}^p - \mathbf{r}_A^c|} - \sum_{i}^{N_e}\frac{1}{|\mathbf{r}_i^e - \mathbf{r}^p|} \quad (1)$$

where all quantities are in atomic units. The coordinates of the electrons, positron, and classical nuclei are denoted as $\mathbf{r}_i^e$, $\mathbf{r}^p$, and $\mathbf{r}_A^c$, respectively. The charges on the classical nuclei, which are represented as point charges, are denoted by $\{Z_A\}$. The indices i, j refer to electrons, and the index A refers to classical nuclei.

Our ansatz for the explicitly correlated electronic−positronic wave function is[28,29]

$$\Psi_{tot} = \Phi^e\chi^p[1 + G] \quad (2)$$

where Φ^e is the electronic Slater determinant comprised of one-electron spin orbitals, χ^p is the positron orbital, and G is the Gaussian-type geminal expansion that explicitly couples the electrons and the positron:

$$G = \sum_{i=1}^{N_e}\sum_{k=1}^{N_{gem}} b_k \exp[-\gamma_k|\mathbf{r}_i^e - \mathbf{r}^p|^2] = \sum_{i=1}^{N_e} g(\mathbf{r}_i^e, \mathbf{r}^p) \quad (3)$$

Here N_{gem} is the number of Gaussians in the expansion, and b_k and γ_k are parameters that can be determined variationally. Note that this form of the wave function includes explicit electron−positron correlation but does not include explicit electron−electron correlation.

The total energy of a multielectron system containing one positron is given by

$$E = \frac{\langle\Psi_{tot}|\hat{H}|\Psi_{tot}\rangle}{\langle\Psi_{tot}|\Psi_{tot}\rangle} \quad (4)$$

This energy expression contains two types of parameters that may be optimized to minimize the energy variationally. The first type of parameter is comprised of the expansion coefficients for the electronic and positronic spatial molecular orbitals, which are typically expanded in terms of atomic orbital Gaussian basis functions. The second type of parameter is comprised of the b_k and γ_k parameters defining the Gaussian-type geminal expansion given in eq 3. To optimize the molecular orbital expansion coefficients, we have derived modified Hartree−Fock−Roothaan equations using the standard variational method to minimize the energy in eq 4 with respect to both the electronic and positronic molecular orbitals subject to the orthonormalization constraints on these orbitals. The analogous Hartree−Fock−Roothaan equations for a many-electron system with one quantum proton are given in ref 29 and are easily modified for positronic systems. For fixed values of the geminal parameters, these equations are solved iteratively to self-consistency to obtain the NEO-XCHF energy. The relatively small number of b_k and γ_k parameters defining the geminal expansion may be optimized numerically on the NEO-XCHF energy surface using a method such as simplex.

The two-photon annihilation rate for any bound state wave function Ψ_0 representing a system consisting of N_e paired electrons in closed shells and a single positron is given by[30,31]

$$\lambda = 4\pi r_0^2 c\,\langle\Psi_0|\sum_{i=1}^{N_e}\delta(\mathbf{r}_i^e - \mathbf{r}^p)\hat{O}_{e_i p}|\Psi_0\rangle \quad (5)$$

where r_0 is the classical electron radius and c is the speed of light. The integration is over the positronic coordinate $\mathbf{r}^p$ and all electronic coordinates. The operator

$$\hat{O}_{e_ip} = \left(1 - \frac{1}{2}\hat{S}^2_{e_ip}\right)$$

is the spin projection operator to the singlet state of the *i*th electron−positron pair. The derivation of the expression for the two-photon annihilation rate based on the NEO-XCHF wave function given in eq 2 is provided in the Appendix.

III. Results

We calculated the total energy and two-photon annihilation rate for PsH with the even-tempered electronic and positronic basis sets developed for this system in ref 27. Each basis set contains a set of s-type Gaussian basis functions with even-tempered parameters[32] variationally optimized at the NEO-MP2 level of theory. The *k*th exponent of the set of Gaussian primitives is $\zeta_k = \alpha\beta^k$, where $\alpha = 0.018298$ Bohr^{-2} and $\beta = 2.66531$ for the electronic basis functions and $\alpha = 0.012420$ Bohr^{-2} and $\beta = 3.91161$ for the positronic basis functions. We variationally optimized the b_k and γ_k parameters defining the geminal expansion in eq 3 for $N_{\text{gem}} = 1-4$ with the 6s/6s electronic/positronic basis set using a post-simplex optimization approach.[33] For $N_{\text{gem}} = 1-3$, we performed a full optimization of all geminal parameters simultaneously starting from many different sets of initial parameter values. For $N_{\text{gem}} = 4$, we performed a more limited optimization in which we started with the results from $N_{\text{gem}} = 3$ and optimized only the fourth pair of geminal parameters, and then we cycled through the four Gaussians in the expansion and optimized each pair of geminal parameters separately. The optimized values of the geminal parameters are given in Table 1.

Table 2 presents the total energies and annihilation rates calculated with the optimized Gaussian-type geminal functions from Table 1 and various electronic and positronic basis sets. As mentioned above, we optimized the geminal parameters using a 6s/6s basis set, corresponding to six s-type Gaussian basis functions for the electrons and the positrons. Using these optimized geminal parameters, we increased the basis sets and determined that the results improve slightly with the 9s/6s basis set, corresponding to nine basis functions for the electrons and six basis functions for the positrons, but do not improve further within numerical accuracy with the 9s/9s basis set. We also observed that the NEO-HF results with these basis sets are similar to those obtained in ref 27 using even-tempered basis sets with s-, p-, and d-type Gaussian basis functions variationally optimized at the NEO-FCI (full configuration interaction) level of theory. We expect that s-type Gaussian basis functions are sufficient to describe the ground-state electronic−positronic wave function because for a single fixed nucleus the two electrons and the positron are expected to occupy s-orbitals. Thus, Table 2 indicates that the results are nearly converged with four geminal functions and the 9s/6s basis set for the NEO-XCHF ansatz for the wave function.

TABLE 1: Values for Parameters (a.u.) Defining the Gaussian-Type Geminal Functions Optimized with the 6s/6s Basis Set

N_{gem}	b_1	γ_1	b_2	γ_2	b_3	γ_3	b_4	γ_4
1	0.805	0.179						
2	1.051	0.042	1.544	0.617				
3	25.436	0.034	22.550	0.624	13.002	5.334		
4	73.992	0.029	61.761	0.504	37.538	2.975	16.191	16.042

TABLE 2: Total Energies E and Annihilation Rates λ for PsH with Different Basis Sets

	E (a.u.)		λ (ns^{-1})	
method[a]	6s/6s	9s/6s[b]	6s/6s	9s/6s[b]
NEO-HF	−0.664337	−0.665640	0.3189	0.3199
NEO-XCHF 1G	−0.693216	−0.694469	0.6883	0.6898
NEO-XCHF 2G	−0.705863	−0.707095	1.1402	1.1401
NEO-XCHF 3G	−0.712496	−0.713393	2.0122	2.0465
NEO-XCHF 4G	−0.716097	−0.717307	2.0443	2.0662

[a] NEO-XCHF *n*G is with $N_{\text{gem}} = n$, and the basis sets are defined by the number of electronic/positronic basis functions. [b] The 9s/9s results are the same as the 6s/6s results for the energies to within 10^{-5} a.u. and for the rates to within 10^{-4} ns^{-1}.

TABLE 3: Total Energies E and Annihilation Rates λ for PsH

method	E (a.u.)	λ (ns^{-1})
NEO-HF[a]	−0.665640	0.3199
NEO-FCI[b]	−0.758965	0.8993
NEO-XCHF[c]	−0. 717307	2.0662
ECG (ref 24)	−0.789197	2.4714
SVM (ref 21)	−0.789198	2.4714

[a] NEO-HF result with the 9s/6s basis set. [b] NEO-FCI result with the 6s3p1d basis set.[27] [c] NEO-XCHF result with four geminal functions and the 9s/6s basis set. The positron is bound to H$^-$ by 6.3 eV at this level of theory.

Table 3 provides a comparison of the NEO-XCHF result with four geminal functions and the 9s/6s basis set to other values previously calculated. The NEO-FCI results from ref 27 obtained with a considerably larger 6s3p1d basis set are provided. In addition, Table 3 presents highly accurate results from the literature: the well-converged stochastic variational method calculations of Mitroy[21] and the variational calculations with explicitly correlated Gaussian functions of Bubin and Adamowicz.[24] These results are viewed as the benchmark value.

The NEO-XCHF energy is not as low as the NEO-FCI energy, but the NEO-XCHF annihilation rate is significantly more accurate than the NEO-FCI annihilation rate. Specifically, the NEO-XCHF annihilation rate is within 20% of the benchmark value, whereas the NEO-FCI annihilation rate is nearly three times smaller than the benchmark value. The NEO-FCI energy is lower than the NEO-XCHF energy mainly because theNEO-FCImethodincludeselectron−electronaswellaselectron−positron correlation, whereas the NEO-XCHF method includes only electron−positron dynamical correlation. The NEO-XCHF method leads to more accurate annihilation rates because the annihilation rate is a measure of the local property of the wave function in the region of small electron−positron distances, where the electron−positron dynamical correlation is most significant and is well-described by the explicitly correlated geminal wave function. The NEO-FCI method provides a more globally accurate wave function, leading to a lower total energy, but does not describe the local properties of the wave function as well as the NEO-XCHF method. Thus, the NEO-XCHF method is particularly well-suited for calculating the annihilation rates, which can be compared to experimental measurements. A method that can predict qualitatively accurate annihilation rates is still useful even if the total energy is not highly accurate because the annihilation rate can be measured experimentally and is relevant for technological applications.

The best NEO-XCHF result for the annihilation rate is within 20% of the most accurate calculations and was calculated at a fraction of the computational costs. For instance, the calculations of Bubin and Adamowicz[24] involved numerical variational optimization of parameters for at least 500 explicitly correlated

Gaussian functions and as many as 5000 functions for the most accurate result presented, while the qualitatively accurate NEO-XCHF calculation required a direct iterative variational optimization of only 12 molecular orbital coefficients and numerical variational optimization of six geminal parameters. The main source of error in the NEO-XCHF annihilation rate is due to the neglect of electron−electron correlation. In addition, the NEO-XCHF approach neglects some three-body effects, although three-particle terms are included in the energy expression. As stated in the Introduction, our objective is not to obtain the most accurate results but rather to obtain qualitatively accurate annihilation rates with a computationally efficient approach that will enable us to study larger systems. The present results indicate that qualitatively accurate positron annihilation rates can be calculated treating only electron−positron correlation explicitly, leading to significant computational savings by neglecting electron−electron dynamical correlation.

IV. Conclusions

In this paper, we used the positronic extension of the NEO-XCHF method to calculate the positron annihilation rate for PsH. The calculated annihilation rate is within 20% of the most accurate values available. The NEO-XCHF method is more computationally efficient than the explicitly correlated methods previously applied to this system because only the electron−positron dynamical correlation is treated explicitly, so fewer parameters must be optimized during the variational procedure. Thus, the NEO-XCHF approach could potentially enable the calculation of qualitatively accurate positron annihilation rates for larger positron systems. Given the wide range of experimentally measured positron annihilation rates for molecular systems,[7,8] such qualitative predictions are expected to be useful for biomedical and technological applications.

A number of potential challenges will arise upon the extension of the NEO-XCHF approach to more complex systems. For some systems, multiconfigurational wave functions may be required to include static correlation. Our recent density matrix formulation of the NEO-XCHF approach[34] allows the use of more general forms of the wave functions, such as open-shell and multireference wave functions. Another issue that could arise is the lack of size-extensivity for calculating binding energies in larger systems. This issue could be problematic for calculating the energetics of a neutral positronium binding to larger systems but will not be problematic for the more experimentally relevant case of a charged positron binding to larger systems. In addition, the use of methods that combine two or more quantum mechanical levels, such as the fragment molecular orbital method,[35] may be required for the study of more complex systems.

Further computational savings could be achieved using multicomponent density functional theory (DFT) in conjunction with an electron−positron functional derived from the explicitly correlated wave function. This type of NEO-DFT approach has been successfully applied to multicomponent systems involving quantum electrons and protons.[36] Another advantage of NEO-DFT is that electron−electron correlation can be included in a computationally efficient and consistent manner,[37] thereby enhancing the accuracy of the calculations. These future research directions are aimed at enabling theoretical calculations on experimentally relevant positron systems.

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Appendix

One-Positron, Many-Electron NEO-XCHF Annihilation Rate. The two-photon annihilation rate for any bound-state wave function Ψ_0 for a system with N_e electrons and a single positron is given in eq 5. This annihilation rate is proportional to the expectation value of the delta function of all electron−positron distances

$$\lambda \propto \langle \Psi_0 | \sum_{i=1}^{N_e} \delta_{e_i p} \hat{O}_{e_i p} | \Psi_0 \rangle \tag{A1}$$

where $\delta_{e_i p} \equiv \delta(\mathbf{r}_i^e - \mathbf{r}^p)$. Using the NEO-XCHF wave function in eq 2, this expectation value can be expressed as

$$\begin{aligned}\langle \Psi_{tot} | \sum_{i=1}^{N_e} \delta_{e_i p} \hat{O}_{e_i p} | \Psi_{tot} \rangle &= \langle \Phi^e \chi^p | \sum_{i=1}^{N_e} \delta_{e_i p} \hat{O}_{e_i p} [1 + 2G + G^2] | \Phi^e \chi^p \rangle \\ &= \sum_{i=1}^{N_e} \langle \Phi^e \chi^p | \Omega_1(\mathbf{r}_i^e, \mathbf{r}^p) \hat{O}_{e_i p} | \Phi^e \chi^p \rangle + \\ &\quad \sum_{i \neq j}^{N_e} \langle \Phi^e \chi^p | \Omega_2(\mathbf{r}_i^e, \mathbf{r}_j^e, \mathbf{r}^p) \hat{O}_{e_i p} | \Phi^e \chi^p \rangle + \\ &\quad \sum_{i \neq j \neq k}^{N_e} \langle \Phi^e \chi^p | \Omega_3(\mathbf{r}_i^e, \mathbf{r}_j^e, \mathbf{r}_k^e, \mathbf{r}^p) \hat{O}_{e_i p} | \Phi^e \chi^p \rangle\end{aligned} \tag{A2}$$

where the one-, two-, and three-particle operators resulting from combining the delta function operator $\delta_{e_i p}$ and the geminal operator

$$g_{e_i p} \equiv \sum_{k=1}^{N_{gem}} b_k \exp[-\gamma_k |\mathbf{r}_i^e - \mathbf{r}^p|^2]$$

are defined as

$$\Omega_1(\mathbf{r}_i^e, \mathbf{r}^p) = \delta_{e_i p}[1 + 2g_{e_i p} + g_{e_i p}^2] \tag{A3}$$

$$\Omega_2(\mathbf{r}_i^e, \mathbf{r}_j^e, \mathbf{r}^p) = \delta_{e_j p}[2g_{e_i p} + g_{e_i p}^2 + 2g_{e_i p} g_{e_j p}] \tag{A4}$$

$$\Omega_3(\mathbf{r}_i^e, \mathbf{r}_j^e, \mathbf{r}_k^e, \mathbf{r}^p) = g_{e_i p} g_{e_j p} \delta_{e_k p} \tag{A5}$$

We now provide the explicit expressions for these terms using the restricted Hartree−Fock (RHF) formulation for closed-shell electron systems. In general, each spin orbital is expressed as the product of a spatial orbital and a spin function. In the RHF formulation, each electronic spatial orbital is doubly occupied, resulting in $N_e/2$ doubly occupied spatial orbitals. In this case, the terms in eq A2 can be expressed as summations of integrals in the basis of electronic spatial orbitals Ψ_α^e and the positronic spatial orbital Ψ^p. The spin projection operator

$$\hat{O}_{e_i p} = \left(1 - \frac{1}{2}\hat{S}_{e_i p}^2\right)$$

leads to the retention of only the electronic spin orbitals with the opposite spin as the positron. The one-particle term is

$$\sum_{i=1}^{N_\mathrm{e}} \langle \Phi^\mathrm{e}\chi^\mathrm{p} | \Omega_1(\mathbf{r}_i^\mathrm{e}, \mathbf{r}^\mathrm{p}) \hat{O}_{\mathrm{e}_i\mathrm{p}} | \Phi^\mathrm{e}\chi^\mathrm{p} \rangle = \sum_{a=1}^{N_\mathrm{e}/2} \Omega_1^{aa} \tag{A6}$$

where

$$\Omega_1^{\mathrm{aa}} = \int\int \mathrm{d}\mathbf{r}_1^\mathrm{e}\, \mathrm{d}\mathbf{r}^\mathrm{p}\, \Omega_1(\mathbf{r}_1^\mathrm{e}, \mathbf{r}^\mathrm{p})[\psi_a^\mathrm{e}(\mathbf{r}_1^\mathrm{e})]^2[\psi^\mathrm{p}(\mathbf{r}^\mathrm{p})]^2 \tag{A7}$$

The two-particle term is

$$\sum_{i\neq j}^{N_\mathrm{e}} \langle \Phi^\mathrm{e}\chi^\mathrm{p} | \Omega_2(\mathbf{r}_i^\mathrm{e}, \mathbf{r}_j^\mathrm{e}, \mathbf{r}^\mathrm{p}) \hat{O}_{\mathrm{e}_i\mathrm{p}} | \Phi^\mathrm{e}\chi^\mathrm{p} \rangle = \sum_{a\neq b}^{N_\mathrm{e}/2} [\Omega_2^{abab} - \Omega_2^{abba}] \tag{A8}$$

where

$$\Omega_2^{abab} = \int\int\int \mathrm{d}\mathbf{r}_1^\mathrm{e}\, \mathrm{d}\mathbf{r}_2^\mathrm{e}\, \mathrm{d}\mathbf{r}^\mathrm{p}\, \Omega_2(\mathbf{r}_1^\mathrm{e}, \mathbf{r}_2^\mathrm{e}, \mathbf{r}^\mathrm{p}) \times [\psi_a^\mathrm{e}(\mathbf{r}_1^\mathrm{e})]^2[\psi_b^\mathrm{e}(\mathbf{r}_2^\mathrm{e})]^2[\psi^\mathrm{p}(\mathbf{r}^\mathrm{p})]^2 \tag{A9}$$

$$\Omega_2^{abba} = \int\int\int \mathrm{d}\mathbf{r}_1^\mathrm{e}\, \mathrm{d}\mathbf{r}_2^\mathrm{e}\, \mathrm{d}\mathbf{r}^\mathrm{p}\, \Omega_2(\mathbf{r}_1^\mathrm{e}, \mathbf{r}_2^\mathrm{e}, \mathbf{r}^\mathrm{p}) \times \psi_a^\mathrm{e}(\mathbf{r}_1^\mathrm{e})\psi_b^\mathrm{e}(\mathbf{r}_2^\mathrm{e})\psi_b^\mathrm{e}(\mathbf{r}_1^\mathrm{e})\psi_a^\mathrm{e}(\mathbf{r}_2^\mathrm{e})\, [\psi^\mathrm{p}(\mathbf{r}^\mathrm{p})]^2 \tag{A10}$$

The three-particle term is

$$\sum_{i\neq j\neq k}^{N_\mathrm{e}} \langle \Phi^\mathrm{e}\chi^\mathrm{p} | \Omega_3(\mathbf{r}_i^\mathrm{e}, \mathbf{r}_j^\mathrm{e}, \mathbf{r}_k^\mathrm{e}, \mathbf{r}^\mathrm{p}) \hat{O}_{\mathrm{e}_i\mathrm{p}} | \Phi^\mathrm{e}\chi^\mathrm{p} \rangle = \sum_{a\neq b\neq c}^{N_\mathrm{e}/2} [\Omega_3^{abcabc} - \Omega_3^{abcbac} + \Omega_3^{cabbac} - \Omega_3^{cabacb} + \Omega_3^{cabbca} - \Omega_3^{cabcba}] \tag{A11}$$

where

$$\Omega_3^{cabbca} = \int\int\int\int \mathrm{d}\mathbf{r}_1^\mathrm{e}\, \mathrm{d}\mathbf{r}_2^\mathrm{e}\, \mathrm{d}\mathbf{r}_3^\mathrm{e}\, \mathrm{d}\mathbf{r}^\mathrm{p}\, \Omega_3(\mathbf{r}_1^\mathrm{e}, \mathbf{r}_2^\mathrm{e}, \mathbf{r}_3^\mathrm{e}, \mathbf{r}^\mathrm{p}) \times \psi_c^\mathrm{e}(\mathbf{r}_1^\mathrm{e})\psi_a^\mathrm{e}(\mathbf{r}_2^\mathrm{e})\psi_b^\mathrm{e}(\mathbf{r}_3^\mathrm{e})\psi_b^\mathrm{e}(\mathbf{r}_1^\mathrm{e})\psi_c^\mathrm{e}(\mathbf{r}_2^\mathrm{e})\psi_a^\mathrm{e}(\mathbf{r}_3^\mathrm{e})[\psi^\mathrm{p}(\mathbf{r}^\mathrm{p})]^2 \tag{A12}$$

and the remaining Ω_3 integrals are defined analogously.

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