Modeling Positrons in Molecular Electronic Structure Calculations with the Nuclear-Electronic Orbital Method

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The nuclear-electronic orbital (NEO) method was modified and extended to positron systems for studying mixed positronic−electronic wavefunctions, replacing the mass of the proton with the mass of the positron. Within the modified NEO framework, the NEO-HF (Hartree−Fock) method provides the energy corresponding to the single-configuration mixed positronic−electronic wavefunction, minimized with respect to the molecular orbitals expressed as linear combinations of Gaussian basis functions. The electron−electron and electron−positron correlation can be treated in the NEO framework with second-order perturbation theory (NEO-MP2) or multiconfigurational methods such as the full configuration interaction (NEO-FCI) and complete active space self-consistent-field (NEO-CASSCF) methods. In addition to implementing these methods for positronic systems, strategies for calculating electron−positron annihilation rates using NEO-HF, NEO-MP2, and NEO-FCI wavefunctions were also developed. To apply the NEO method to the positronium hydride (PsH) system, positronic and electronic basis sets were optimized at the NEO-FCI level and used to compute NEO-MP2 and NEO-FCI energies and annihilation rates. The effects of basis set size on NEO-MP2 and NEO-FCI correlation energies and annihilation rates were compared. Even-tempered electronic and positronic basis sets were also optimized for the e^+LiH molecule at the NEO-MP2 level and used to compute the equilibrium bond length and vibrational energy.

1. Introduction

Dirac predicted the existence of the positron as the antiparticle of the electron in 1928.[1] In 1932, the first experimental indications of an unknown particle were found in cloud-chamber photographs of cosmic rays, and this particle was later identified as the positron. Annihilation of the positron with electrons in matter was studied in the 1940s. An important early discovery was that energy and momentum conservation during the annihilation process could be utilized to study properties of solids.[2] Recent advances in the use of trap-based, slow positron beam sources have enabled the study of low-energy positron interactions with atoms and molecules.[3,4] Energy-resolved measurements of Barnes et al.[4] present direct evidence for the enhancement of annihilation rates due to the existence of vibrational Feshbach resonances. These experimental data provide motivation for the development of efficient computational methods for the study of positronic systems.

A variety of computational methods have been employed to accurately compute positron and positronium binding to atoms.[5] The PsH system, consisting of a proton, two electrons, and a positron, was studied with restricted Hartree−Fock[6] and configuration interaction (CI) methods[7] in the 1960s. In 1970, Schrader presented a self-consistent-field theory for one-positron many-electron systems that included electron−positron correlation explicitly in the electronic molecular orbitals (MOs).[8] Kurtz and Jordan[9] studied positron-molecule complexes with Hartree−Fock (HF) theory in 1981. More recently, the quantum Monte Carlo method,[10] the stochastic variational method,[11,12] a perturbative geminal approach,[13] explicitly correlated Gaussian variational approaches,[14,15] and various configuration interaction (CI) approaches[16−21] have been used to study PsH and other small molecular positronic systems. In addition, Bubin and Adamowicz have applied a highly accurate variational approach using explicitly correlated Gaussian functions to PsH and e^+-LiH.[22,23] Although these approaches have achieved impressive levels of accuracy, they are not easily extended to larger positronic systems.

The objective of the present work is to introduce and illustrate a modified nuclear-electronic orbital (NEO) method for calculations of positronic−electronic systems. The NEO approach was developed to include nuclear quantum effects directly within electronic structure calculations and has been successfully applied to proton transfer and hydrogen tunneling problems.[24−32] In the extension of the NEO method to positronic systems, the positrons are treated quantum mechanically on the same level as the electrons. At the NEO-HF level of theory, mixed positronic−electronic wavefunctions are calculated iteratively using variational MO techniques. Electron−electron and electron−positron correlation can be included by second-order perturbation theory (NEO-MP2), the complete active space self-consistent field (NEO-CASSCF) method, and the full configuration interaction (NEO-FCI) approach. In addition to implementing all of these methods, we derived the expressions for

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calculating electron−positron annihilation rates based on NEO-HF, NEO-MP2, and NEO-FCI wavefunctions.

To illustrate the NEO method, we applied it to the PsH system and to the e^+LiH system. Both of these systems have been studied previously with a variety of computational methods.[6−23,33] The NEO approach is not expected to be more accurate than these other methods but is designed to be more easily extendable to larger systems. For the PsH system, we optimized positronic and electronic Gaussian basis sets at the NEO-FCI level. These basis sets were subsequently used to compute NEO-MP2 energies for PsH. We also assessed the basis set dependence of the total energies and the electron−electron and electron−positron correlation energies at the NEO-MP2 and NEO-FCI levels. For the e^+LiH system, we optimized even-tempered electronic and positronic Gaussian basis sets for PsH and Li at the NEO-MP2 and MP2 levels, respectively. At the same level of theory with a reoptimized positronic basis set, we mapped the potential energy surface for e^+LiH and calculated the equilibrium geometry and the shift of the vibrational frequency caused by addition of a positron to LiH.

2. Theory and Computational Method

2.1. Modifications to the NEO Formulation. The original NEO method, which was incorporated into a recent version of the GAMESS code,[34] includes nuclear quantum effects directly within electronic structure calculations. It has been used mainly to treat protons quantum mechanically. For simplicity, here we consider the special case of systems with N_e paired electrons, a single quantum proton, and N_c classical nuclei. The extension to multiple quantum nuclei is straightforward. In this case, the Hamiltonian is

$$\hat{H} = -\sum_i^{N_e} \frac{1}{2}\nabla_i^2 - \frac{1}{2m_p}\nabla_{1'}^2 - \sum_A^{N_c}\sum_i^{N_e}\frac{Z_A}{r_{iA}} + \sum_A^{N_c}\frac{Z_A}{r_{1'A}} + \sum_i^{N_e}\sum_{j>i}^{N_e}\frac{1}{r_{ij}} - \sum_i^{N_e}\frac{1}{r_{i1'}} \quad (1)$$

where the unprimed indices i and j refer to electrons, the primed indices i' and j' refer to quantum protons, the index A refers to classical nuclei, and m_p is the proton mass. The charges and distances are denoted by Z and r, respectively, with the appropriate subscripts.

In the NEO-HF approach, the nuclear-electronic wavefunction is the product of an electronic and a nuclear Slater determinant

$$\Psi_{\mathrm{HF}}(\mathbf{r}^e,\mathbf{r}^p) = \Phi^e(\mathbf{r}^e)\Phi^p(\mathbf{r}^p) \quad (2)$$

Here $\mathbf{r}^e$ represents all electronic coordinates, $\mathbf{r}_i^e$ will represent the coordinate of the ith electron, and $\mathbf{r}^p$ represents the coordinate of the single quantum proton. For the case of a single quantum proton, the nuclear Slater determinant is a nuclear MO. In the NEO-HF approach, the energy is minimized variationally with respect to the electronic and nuclear MOs, which are expanded in Gaussian basis sets. The MP2 corrections to the NEO-HF energy are derived in ref 28. These previous studies illustrate that eq 1 is a suitable reference Hamiltonian for NEO-MP2 calculations. The NEO-CASSCF and NEO-CI formulations are presented in ref 24.

In principle, modifying the NEO method in GAMESS for the calculation of positronic systems is as simple as substituting the proton's mass with that of the positron. The initial implementation of NEO in GAMESS was developed to model quantum effects for nuclei, however, and does not allow nuclear basis functions to be centered on classical nuclei, where the electronic basis functions are located. Due to the nature of the positronic wavefunction, the optimal configuration for positronic basis functions is to be centered on classical nuclei with the electronic basis functions. The code was modified to allow for this situation in the extension of the NEO method for the calculation of mixed positronic−electronic wavefunctions.

The resulting modified NEO approaches for positronic systems are analogous to their counterparts for quantum nuclear systems. In the modified NEO-HF method, the energy corresponding to the single-configurational mixed positronic-electronic wavefunction is minimized with respect to the MOs. In the NEO-CASSCF method, the energy is minimized with respect to the MOs, as well as the CI coefficients, including all possible CI configurations that result from the chosen positronic and electronic active spaces in an analogous manner to the existing electronic structure method CASSCF. Within the NEO-CASSCF framework, if all of the quantum particles (i.e., electrons and positrons) in the system are active and the active space includes all of the available MOs, then the calculation is termed NEO-FCI. In this case, the energy is minimized with respect to only the CI coefficients. Dynamical electron−electron and electron−positron correlation effects can also be included in the NEO framework using second-order perturbation theory (NEO-MP2).

2.2. Positron Basis Set Development. In addition to modifying the existing NEO code in GAMESS, new positronic and modified electronic basis sets were needed before applying NEO to a molecular positronic−electronic system. For PsH, we optimized the basis function exponents in [6s], [6s1p], [6s2p], [6s3p], [6s2p1d], and [6s3p1d] basis sets for both electrons and the positron at the NEO-FCI level, using the same size basis sets for the electronic and positronic wavefunctions. These particular basis set sizes were chosen for direct comparison to results of Tachikawa,[16] in which basis function exponents for both electrons and the positron were optimized using a fully variational CI method. The optimized electronic and positronic basis sets for PsH were then used to compute NEO-MP2 and NEO-FCI energies. The effect of the basis set size on the amount of electron−electron and electron−positron correlation energy captured is discussed in section 3.

We also developed even-tempered electronic and positronic basis sets for Li and PsH, respectively, at the MP2 and NEO-MP2 levels, respectively. Note that the variational theorem does not apply to the second-order perturbation theory energy, which is not an expectation value of the Hamiltonian. Nevertheless, as noted previously,[35] this method is useful for including correlation in basis set development. In the even-tempered scheme, the radial functions of the primitives are chosen such that the kth exponent, $\zeta_{k,l}$ of the set of Gaussian primitives of symmetry type l is specified with the even-tempered parameters α_l and β_l^k by the equation

$$\zeta_{k,l} = \alpha_l\beta_l^k \quad (3)$$

Starting with an even-tempered basis on H^- and Li consisting of six s-type Gaussian primitives [6s], α_s and β_s were optimized with respect to the MP2 energy using the QDFIT2 program.[36] This optimization procedure was similar to that of Schmidt and Ruedenberg in that Gaussian primitives of each type were systematically added to the basis set until the improvement in the MP2 energy fell below a specified threshold. This initial basis set was then expanded by adding s-functions, one at a time, and the α_s and β_s were re-optimized using the optimum parameters from the previous iteration as the initial guess. The shell was considered full when the MP2 energy decreased by less than 0.1 milli-Hartree. This procedure was then repeated for p-and d-type Gaussian primitives, beginning with three functions in each of the higher angular momentum shells. All even-tempered parameters were optimized at each step. Thus, the final step involved a six-parameter optimization (i.e., α and β for s, p, and d-type Gaussian primitives) for each electronic basis set. In some instances where four or more even-tempered parameters were optimized, the potential energy surface was found to be very flat, and the QDFIT2 program did not find the minimum of the MP2 energy. For these cases, we used the Hooke-Jeeves generalized pattern search algorithm, implemented in the GenOpt program,[37] to locate the optimum α's and β's.

The even-tempered electronic and positronic basis sets for PsH were then optimized by starting with the electronic basis sets developed for H^- and an initial even-tempered positronic basis set consisting of three s-type Gaussian primitives [3s]. The positronic basis set size was then increased using the same methodology as prescribed above while the electronic basis set size was held fixed at the size optimized for H^-. All even-tempered parameters for both electrons and positrons were optimized at each step, ultimately resulting in a 12-parameter optimization (i.e., α and β for s, p, and d-type Gaussian primitives for electrons and positrons) to obtain the final mixed positronic−electronic basis sets. After the optimum positronic basis set size was found for PsH, we increased the electronic basis set size in each shell and re-optimized the parameters to confirm that the electronic basis set size was still optimum. We found this to be the case. The resulting even-tempered basis sets were used to compute the optimized geometry and vibrational frequency of e^+LiH.

2.3. Annihilation Rate. Using mixed positronic−electronic wavefunctions obtained with the NEO method, electron−positron annihilation rates can be computed at the NEO-HF, NEO-MP2, and NEO-FCI levels. Neglecting three-photon annihilation, the electron−positron annihilation rate for a bound state wavefunction, Ψ_0, consisting of N_e electrons and a single positron is given by[38]

$$\lambda = \pi {r_0}^2 c \int \sum_{i=1}^{N_e} \delta(\mathbf{r}_i^{\,e} - \mathbf{r}^p) |\Psi_0(\mathbf{r}^e, \boldsymbol{r}^p)|^2 \, \mathrm{d}\mathbf{r}^e \, \mathrm{d}\mathbf{r}^p \tag{4}$$

where the integration is over all electronic coordinates and the positronic coordinate. For simplicity, the equations in this paper are given for systems with a single positron, but the extension to systems with multiple positrons is straightforward.

At the NEO-HF level, for N doubly occupied electronic MOs, eq 4 simplifies to

$$\lambda^{HF} = 2\pi {r_0}^2 c \sum_{i=1}^{N} S_{ii1'1'} \tag{5}$$

where $S_{iji'j'}$ is the four-center integral

$$S_{iji'j'} = \int \phi_i(\mathbf{r}) \phi_j(\mathbf{r}) \phi_{i'}(\mathbf{r}) \phi_{j'}(\mathbf{r}) \, \mathrm{d}\mathbf{r} \tag{6}$$

in which $r = r^e = r^p$, r_0 is the classical electron radius, c is the speed of light, and $\phi_{i(i')}$ is the $i(i')$th electron (positron) MO. Again, we use unprimed (primed) indices to denote electron (positron) MOs. Note that the spatial coordinates in the four MOs in eq 6 are the same because of the Dirac delta function in eq 4, and $S_{iji'j'}$ has units of a.u.$^{-3}$.

Within the NEO-MP2 framework, the first-order correction to the annihilation rate is

$$\lambda^{(1)} = -\,4\pi {r_0}^2 c \sum_{arr'} \frac{\langle a1'|rr'\rangle}{\varepsilon_a + \varepsilon_{1'} - \varepsilon_r - \varepsilon_{r'}} S_{ar1'r'} \tag{7}$$

where the summation is over the RHF (restricted Hartree−Fock) occupied and virtual electron MOs (a and r, respectively) and the virtual positron MOs (r'). $\varepsilon_{i(i')}$is the eigenvalue for the ith (i'th) electron (positron) MO, and $\langle ii'|jj'\rangle$ is the electron−positron Coulomb integral

$$\langle ii'|jj'\rangle = \int \phi_i(\mathbf{r}^e) \phi_{i'}(\mathbf{r}^p) r_{ep}^{-1} \phi_j(\mathbf{r}^e) \phi_{j'}(\mathbf{r}^p) \, \mathrm{d}\mathbf{r}^{\boldsymbol{e}} \, \mathrm{d}\mathbf{r}^p \tag{8}$$

The NEO-MP2 annihilation rate is then given by $\lambda^{MP2} = \lambda^{HF} + \lambda^{(1)}$.

The NEO-CI wavefunction has the form

$$\Psi_{tot}(\mathbf{r}^e, \mathbf{r}^p) = \sum_{I}^{N_{CI}^e} \sum_{I'}^{N_{CI}^p} C_{II'} \Phi_I^e(\mathbf{r}^e) \Phi_{I'}^p(\mathbf{r}^p) \tag{9}$$

where $\Phi_I^e(\mathbf{r}^e)$ and $\Phi_{I'}^p(\mathbf{r}^p)$ are determinants of spin orbitals representing the electrons and positron, respectively, and $C_{II'}$ are CI coefficients. Here there are N_{CI}^e electronic determinants and N_{CI}^p positron determinants, leading to a total of $N_{CI} = N_{CI}^e \times N_{CI}^p$ positronic−electronic configurations. For the NEO-CI wavefunction in eq 9 with only a single positron, the annihilation rate is given by

$$\lambda^{CI} = 2\pi {r_0}^2 c \left[\sum_{I}^{N_{CI}^e} \sum_{I',J'}^{N_{CI}^p} C_{II'} C_{IJ'} \sum_{i=1}^{N_e} S_{I_i I_i I' J'} + 2 \sum_{I<J*}^{N_{CI}^e} \sum_{I',J'}^{N_{CI}^p} C_{II'} C_{JJ'} S_{I_i J_j I' J'} \right] \tag{10}$$

Here $\sum_{I<J*}^{N_{\mathrm{CI}}^{\mathrm{e}}}$ denotes a summation over unique pairs of electronic determinants, denoted by the indices I and J, that differ by one and only one MO, corresponding to the MO indices i and j, respectively. In this expression, I_i represents the ith electronic MO of the $\Phi_I^e(\mathbf{r}^e)$ electronic determinant. Since eq 10 is for only a single positron, the indices I' and J' denote the positron MO rather than a determinant. The module for computing annihilation rates based on eqs 5−10 has been incorporated into NEO in GAMESS.

3. Results and Discussion

In a positronic−electronic system, both electron−electron and electron−positron correlation energies substantially impact the total ground state energies and annihilation rates. We investigated how these correlation energies vary between the NEO-MP2 and NEO-FCI methods and with different basis set sizes for PsH. In Table 1, NEO-HF, NEO-MP2, and NEO-FCI energies and annihilation rates are given for PsH with [6s], [6s1p], [6s2p], [6s3p], [6s2p1d], and [6s3p1d] basis sets with exponents optimized at the NEO-FCI level. Also provided are the electron−electron and electron−positron correlation energies recovered with NEO-MP2. The total correlation energy recovered with NEO-MP2 is then compared to the NEO-FCI correlation energy. The annihilation rates are also plotted in Figure 1.

Two significant trends are evident from the data in Table 1 and the plot in Figure 1. As the basis set size is increased, the following trends are observed: (1) the magnitudes of the electron−electron and electron−positron correlation energies increase, providing virtually all of the improvement in the NEO-MP2 and NEO-FCI energies and annihilation rates (i.e., the change in the NEO-HF energy and annihilation rate is negligible), and (2) the fraction of the correlation energy recovered

TABLE 1: Comparison of NEO-MP2 and NEO-FCI Results for PsH[a,b]

	[6s]	[6s1p]	[6s2p]	[6s3p]	[6s2p1d]	[6s3p1d]
E_{HF}	−0.666766	−0.666791	−0.666783	−0.666784	−0.666865	−0.666872
E_{MP2}	−0.683835	−0.715107	−0.721801	−0.723411	−0.726725	−0.728306
E_{FCI}	−0.691010	−0.732176	−0.743336	−0.745807	−0.756408	−0.758965
E_{MP2}^{ee}	−0.010649	−0.020459	−0.024004	−0.025103	−0.025226	−0.026309
E_{MP2}^{ep}	−0.006420	−0.027858	−0.031014	−0.031525	−0.034634	−0.035125
E_{MP2}^{corr}	−0.017070	−0.048316	−0.055018	−0.056628	−0.059860	−0.061435
E_{FCI}^{corr}	−0.024244	−0.065385	−0.076553	−0.079023	−0.089544	−0.092094
$E_{MP2}^{corr}/ E_{FCI}^{corr}$	0.704079	0.738948	0.718686	0.716599	0.668503	0.667083
λ^{HF} (ns^{-1})	0.297218	0.297585	0.297870	0.297660	0.297895	0.297736
λ^{MP2} (ns^{-1})	0.349059	0.464326	0.493770	0.503096	0.528715	0.537651
λ^{FCI} (ns^{-1})	0.372328	0.639403	0.719402	0.751466	0.866199	0.899299

[a] NEO-HF, NEO-MP2, and NEO-FCI energies (E_{HF}, E_{MP2}, and E_{FCI}, respectively) and annihilation rates (λ^{HF}, λ^{MP2}, and λ^{FCI}, respectively) were obtained for PsH with basis sets optimized at the NEO-FCI level. The correlation energy recovered with NEO-MP2 ($E_{MP2}^{corr} = E_{MP2} - E_{HF} = E_{MP2}^{ee} + E_{MP2}^{ep}$) and NEO-FCI ($E_{FCI}^{corr} = E_{FCI} - E_{HF}$), the second-order electron−electron (E_{MP2}^{ee}) and electron−positron (E_{MP2}^{ep}) corrections that comprise the NEO-MP2 correction, and the fraction of the NEO-CI correlation energy recovered with NEO-MP2 ($E_{MP2}^{corr}/E_{FCI}^{corr}$) are also provided. [b] Accurate values of the energies and annihilation rates for PsH are given in the text.

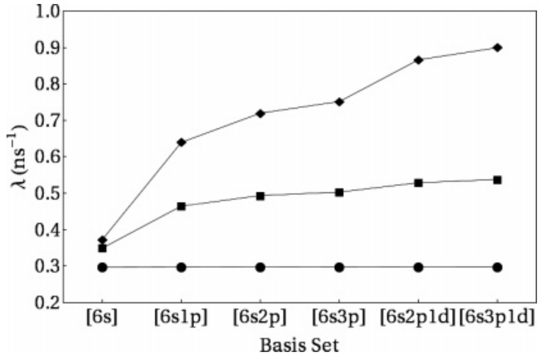

Figure 1. NEO-HF (●), NEO-MP2 (■), and NEO-FCI (♦) annihilation rates for PsH.

with NEO-MP2 versus NEO-FCI decreases slightly. The increasing values for the electron−electron and electron−positron correlation energy seen in the first trend indicate that the larger basis set yields a better set of orbitals for recovery of dynamical correlation through perturbation and multiconfigurational methods. The increase in the electron−positron correlation energy corresponds to an increase in the electron−positron annihilation rate. The second trend illustrates that the increase in the NEO-MP2 correlation energy with basis set size is slower than the increase in the NEO-FCI correlation energy. The multiconfigurational character of the NEO-FCI wavefunction can be determined by examination of the natural orbital occupation numbers (NOONs).[39] The highest NOON value for the positron changes from 0.9872 for the [6s] basis set to 0.8837 for the [6s3p1d] basis, a decrease of 10.4%. This decrease indicates that the NEO-FCI wavefunction becomes more multiconfigurational for this choice of orbitals as the basis set increases.

We also optimized even-tempered basis sets for H$^-$, Li, and PsH using the procedure outlined in section 2.2. The even-tempered parameters are given in Table 2. We found that the optimum electronic basis set sizes are [9s5p4d] and [13s6p4d] for H$^-$ and Li, respectively, and the optimum positronic basis set size for PsH is [6s4p4d]. In general, we found that the optimal electronic and positronic basis sets have approximately the same number of p- and d-type primitives, while the positronic basis set has fewer s-type primitives than the electronic basis set. The NEO-MP2 energy of PsH with the resulting [9s5p4d-6s4p4d] basis set is −0.731866 Hartree, which is 0.00356 Hartree lower than the best NEO-MP2 result achieved with the FCI-optimized basis sets of Table 1; however, it is still 0.027099 Hartree higher than the best NEO-FCI result given.

Subsequent to this even-tempered basis set optimization, we computed the potential energy surface (PES) for e$^+$LiH at the NEO-MP2 level with the Li and PsH even-tempered basis sets. We found that the energy of e$^+$LiH decreased significantly when the even-tempered parameters for the positronic basis set on the hydrogen atom and the internuclear distance were simultaneously optimized to minimize the NEO-MP2 energy. The resulting e$^+$LiH positronic basis set is provided in Table 2.

A summary of the results obtained with the even-tempered basis sets optimized for the LiH and e$^+$LiH systems is provided in Table 3. This table includes the NEO-HF and NEO-MP2 energies, Li−H bond lengths (R_e and R_0), and vibrational energies (ν). Also given is the dissociation energy ($\triangle$) for the lowest-energy dissociation channel, e$^+$LiH → Li$^+$ + PsH. The values of R_e, R_0, and ν were determined by computing the PES along the Li−H distance, R_{LiH}, and fitting the data to a Morse potential, as depicted in Figure 2. The Morse potential was determined with a least-squares fitting method using the data points for 1.25 Å$< R_{LiH} <$ 2.5 Å, and the eigenvalues and eigenfunctions of this Morse potential were computed analytically.[40] The values of R_0 were obtained from the average of R_{LiH} over the ground state vibrational wavefunction, and the vibrational energies were determined from the splitting between the lowest two vibrational states for this Morse potential. The computed values for R_0 and ν of the nonpositronic LiH molecule agree well with the experimental values of 1.5957 Å and 1406 cm^{-1}, respectively.[41] The values of R_0 and ν computed for e$^+$LiH are 1.6691 Å and 1160 cm^{-1}, respectively. Thus, the vibrational energy of e$^+$LiH is computed to be approximately 30 meV less than that of LiH. We calculated the dissociation energy for the e$^+$LiH → Li$^+$ + PsH dissociation channel to be 1.626 eV, which is higher than the dissociation energies of 0.77275 eV calculated with the stochastic variational method,[12] 1.03(7) eV calculated with the quantum Monte Carlo method,[10] and 0.99452 eV calculated with a non-Born−Oppenheimer variational method with explicitly correlated Gaussian functions.[22]

We have also considered whether positron basis functions should be centered on only the more electronegative H atom or on both the H and Li atoms in e$^+$LiH. To explore this issue, we determined optimum electronic and positronic basis sets for LiPs using the same method that was applied to PsH above. Then we determined the optimum positronic molecular basis set and internuclear distance at the NEO-MP2 level for e$^+$LiH,

TABLE 2: H^-, Li, PsH, and e^+LiH Even-tempered Basis Set Parameters and Associated Energies Optimized with MP2 and NEO-MP2 Methods

system	basis	α_s	β_s	α_p	β_p	α_d	β_d	E_{MP2}
H^-	e^- 9s5p4d	0.004082	3.12031	0.018186	2.74250	0.033809	2.77814	−0.516892
Li	e^- 13s6p5d	0.010651	2.65645	0.066641	2.77175	0.329441	2.81975	−7.472392
PsH	e^- 9s5p4d	0.018298	2.66531	0.029626	2.46850	0.041616	2.66534	−0.731866
	e^+ 6s4p4d	0.012420	3.91161	0.029026	2.36631	0.022201	2.55911	
e^+LiH	e^+ 6s4p4d	0.007373	1.76822	0.004573	3.32930	0.016052	2.31927	−8.068859

TABLE 3: LiH and e^+LiH MP2 and NEO-MP2 Results[a]

	E_{HF}	E^{ee}_{MP2}	E^{ep}_{MP2}	E_{MP2}[d]	R_e (Å)	R_0 (Å)[b]	Δ (eV)[c]	ν (cm^{-1})[b]
LiH	−7.987210	−0.069001		−8.056211	1.5892	1.5979		1410
e^+LiH	−7.991805	−0.068397	−0.008657	−8.068859	1.6652	1.6691	1.625510	1164

[a] The Hartree−Fock energies (E_{HF}), MP2 energies (E_{MP2}), and electron−electron and electron−positron correlation contributions to the MP2 energies (E^{ee}_{MP2} and E^{ep}_{MP2}, respectively) are provided. Also given are the bond lengths (R_e and R_0), dissociation energy (△), and vibrational energies (ν). Energies are in Hartrees unless otherwise specified. [b] The experimental LiH bond length and vibrational frequency are 1.5957 Å and 1406 cm^{-1}, respectively.[41] [c] The e^+LiH dissociation energy is computed for the $e^+LiH \rightarrow Li^+ + PsH$ dissociation channel, using an Li^+ MP2 energy of −7.274638 Hartree computed with the Li MP2-optimized [13s6p4d] even-tempered basis set and the PsH NEO-MP2 energy given in Table 2. [d] An accurate value of the energy for e^+LiH is −8.1047 Hartrees.[22]

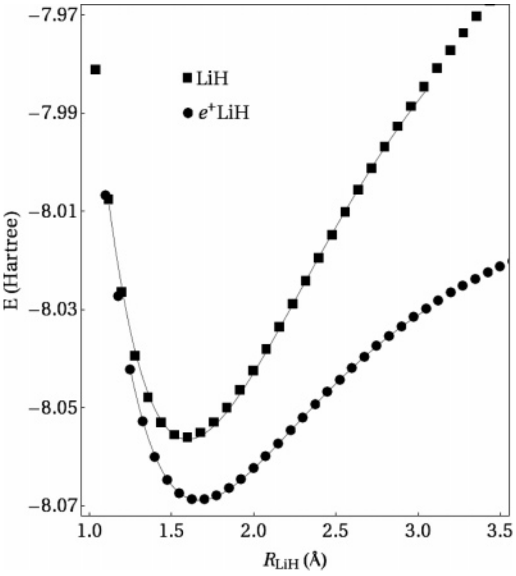

Figure 2. Comparison of LiH and e^+LiH MP2 and NEO-MP2 potential energy surfaces with associated electronic and positronic basis sets from Table 2. The Morse potential fts used to compute the vibrational energies are also shown.

optimizing even-tempered parameters for positronic basis sets on both the H and the Li atoms. The resulting minimum energy was −8.069102 Hartrees, a decrease of only 0.000243 Hartree compared to the calculation with positron basis functions on only the H atom. We also computed the potential energy surface for this system, and the equilibrium bond length and vibrational energy were 1.6673 Å and 1159 cm^{-1}, respectively, which are very close to the numbers obtained previously. From these results, we conclude that for e^+LiH, placement of the positronic basis functions on only the more electronegative hydrogen atom is sufficient at the NEO-MP2 level.

We emphasize that the NEO-FCI and NEO-MP2 methods are not quantitatively accurate tools for computing energies and annihilation rates for positronic systems. Our most reliable NEO-FCI energy and annihilation rate for PsH are −0.758965 Hartree and 0.899299 ns^{-1}, respectively. For comparison, well-converged stochastic variational method calculations provide a PsH energy of −0.78919674 Hartree and an annihilation rate of 2.47178 ns^{-1},[11] and highly accurate variational calculations with explicitly correlated Gaussian functions provide a PsH energy of −0.78919765251 Hartree and an annihilation rate of 2.471406 ns^{-1}.[23] As illustrated in Table 1 and Figure 1, the NEO-FCI annihilation rate converges very slowly with respect to the positronic basis set and is not yet converged in the present work. Mitroy et al.[21,33] have performed more extensive CI calculations on PsH beyond the NEO-FCI calculations presented here and have also identified difficulties with convergence in the application of traditional CI approaches to systems in which electron−positron correlation is important. Perturbative approaches such as NEO-MP2 are even more problematic for these types of systems.

On the other hand, the NEO framework provides a foundation upon which future methods for studying large positronic molecular systems can be built. The quantitative accuracy of the NEO approach may be improved by developing larger positron basis sets and extending the method to include more electron−electron and electron−positron correlation energy. In particular, explicit electron−positron correlation can be included directly into the NEO self-consistent-field framework using Gaussian-type geminals, as implemented in ref 31 for electron−proton correlation. This explicitly correlated Hartree−Fock (NEO-XCHF) approach has been shown to converge much faster than the NEO-FCI approach and is computationally practical for many-electron systems with a relatively small number of positrons because only electron−positron correlation is treated explicitly.

4. Conclusions

Our modified NEO approach provides a potentially useful framework for computing mixed positronic−electronic wavefunctions. We demonstrated its utility by computing the potential energy surface of e^+LiH, allowing the prediction of its equilibrium geometry, vibrational energy, and dissociation energy. We also calculated the energy and the annihilation rate for PsH at the NEO-MP2 and NEO-FCI levels. We compared the amount of electron−electron and electron−positron correlation energy captured with the NEO-MP2 and NEO-FCI methods for PsH. In the process of extending the NEO method for positrons, we demonstrated a systematic approach for developing even-tempered electronic and positronic basis sets for NEO calculations. Basis sets developed using atomic calculations were found to provide a reasonable starting point for molecular calculations. Further optimization of the positronic basis set parameters, however, was necessary to accurately describe the potential energy surface of the molecule. The quantitative accuracy of energy calculations can be improved by the inclusion of explicit electron−positron correlation directly into the NEO self-consistent-field framework using Gaussian-type geminals.[31]

Since the NEO method is implemented in the GAMESS code, it can be coupled to many existing electronic structure methods, including the multi-level methods that are available for studying large systems. In the future, we plan to apply this method to positron spectroscopy for larger molecules. The feedback between theory and experiment will assist in the further improvement of the methodology.

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