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A Variational Monte Carlo Study of Positronic Compounds Using Inhomogeneous Backflow Transformations

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A variational Monte Carlo study using inhomogeneous backflow transformations is reported for the [H^-;e^+] and [Li^-;e^+] positronic compounds. The backflow transformations greatly improve the total energies, positron affinities, and two-photon annihilation rates. The Slater–Jastrow-backflow trial wave function is well suited to the theoretical analysis of positronic compounds.

The positron (e^+) has the same mass and spin as its antiparticle, the electron (e^-), but is of opposite charge. Positrons injected into a liquid or solid induce processes such as ionization or electronic excitation of atoms/molecules, the formation of a metastable bound state of a positron and an electron (positronium, Ps), the formation of positronic molecular complexes, etc., before the positron undergoes pair-annihilation with an electron.[1] Properties such as the electronic/positronic structures and the stable geometry of the positronic molecular complexes cannot, however, be obtained in detail from experiments due to the very short lifetime of such complexes (10^{-7}–10^{-10} s).

Two accurate theoretical approaches are known for studying positronic compounds: variational calculations with explicitly correlated Gaussian (ECG) wave functions[2–4] and ab initio quantum Monte Carlo (QMC) calculations,[5–7] especially the diffusion Monte Carlo (DMC) method. Although variational calculations with ECG wave functions have given the most accurate results obtained to date, this method cannot in practice be applied to larger systems because its computational effort grows much faster with the number of particles than is the case for QMC methods. Ab initio QMC methods are, therefore, well suited to calculations for large positronic complexes. We have obtained accurate energetics for positronic compounds using QMC techniques.[8] However, in evaluating expectation values of operators which do not commute with the Hamiltonian, such as two-photon annihilation rates in positronic compounds, the DMC results depend on the quality of the trial wave function when the standard extrapolated estimation technique is used.[5] Since the Slater–Jastrow trial wave function does not always give adequate results for the two-photon annihilation rate, a more sophisticated trial wave function is required.

In this study, we have applied a parameterized inhomogeneous backflow (BF) transformation[9] to the Slater–Jastrow (SJ) trial wave function for positronic compounds and demonstrated its accuracy in calculations of the total energies, positron affinities, and two-photon annihilation rates of the [H^-;e^+] and [Li^-;e^+] systems. In the backflow transformation, parameters are introduced into the one-electron orbitals of the Slater determinants so that the values of the orbitals also depend on the positions of the other particles. Recently, López Ríos et al.[9] have proposed inhomogeneous backflow transformations for atoms, molecules, and solids. Although they showed that backflow transformations significantly improve the many-body wave functions, the accuracy of the backflow transformation for positronic compounds has not yet been investigated.

The SJ trial wave function for a positronic compound which contains N electrons, M nuclei, and a positron, is

$$\Psi_{\mathrm{T}}^{\mathrm{SJ}}(\mathbf{R}) = \mathrm{e}^{\mathrm{J}(\mathbf{R})} \times \mathrm{D}_{\mathrm{e}}^{\uparrow}(\mathbf{R}_{\mathrm{e}}^{\uparrow})\mathrm{D}_{\mathrm{e}}^{\downarrow}(\mathbf{R}_{\mathrm{e}}^{\downarrow})\varphi_{\mathrm{p}}(\mathbf{r}_{\mathrm{p}}) \qquad (1)$$

where $\mathrm{e}^{\mathrm{J}(\mathbf{R})}$ is the Jastrow factor, $\mathrm{D}_{\mathrm{e}}^{\uparrow\downarrow}$ is the Slater determinant for up/down-spin electrons, and φ_{p} is the positronic orbital. The vector $\mathbf{R} = (\mathbf{R}_{\mathrm{e}}, \mathbf{r}_{\mathrm{p}})$ denotes the configuration in the $3(N+1)$-dimensional space consisting of the electronic configuration $\mathbf{R} = (\mathbf{r}_1, \ldots, \mathbf{r}_N)$ and positronic configuration $\mathbf{r}_{\mathrm{p}}$. We generate the Slater parts of the trial wave function using the multi-component molecular orbital (MC_MO) method within the Hartree–Fock (HF) approximation,[10] where the molecular orbitals of both electrons and positron are expanded as linear combinations of Gaussian-type functions (GTFs). We use 10 s functions for the electrons and for the positron in [H^-;e^+] and 20 s functions for [Li^-;e^+], and the exponents are optimized at the HF level. We use the Jastrow factor developed by Drummond et al. which contains electron–electron, electron–nucleus, and electron–electron–nucleus two- and three-body terms, to which we add electron–positron and electron–positron–nucleus terms.[11] The BF transformations for positronic compounds are introduced by substituting a set of collective coordinates $\mathbf{X}$ for the coordinates $\mathbf{R}$ in the Slater part in eq 1:

$$\Psi_{\mathrm{T}}^{\mathrm{SJB}}(\mathbf{R}) = \mathrm{e}^{\mathrm{J}(\mathbf{R})} \times \mathrm{D}_{\mathrm{e}}^{\uparrow}(\mathbf{X}_{\mathrm{e}}^{\uparrow})\mathrm{D}_{\mathrm{e}}^{\downarrow}(\mathbf{X}_{\mathrm{e}}^{\downarrow})\varphi_{\mathrm{p}}(\mathbf{x}_{\mathrm{p}}) \qquad (2)$$

where $\mathbf{x}_i = \mathbf{r}_i + \xi_i(\mathbf{R})$, and ξ_i is the backflow displacement of particle i, which depends on the positions of the electrons, the nuclei, and the positron. The backflow displacement proposed by López Ríos et al.[9] is a sum of two- and three-body terms: electron–electron ($\xi_i^{\mathrm{e-e}}$), electron–nucleus ($\xi_i^{\mathrm{e-n}}$), and electron–electron–nucleus terms ($\xi_i^{\mathrm{e-e-n}}$). In order to extend the backflow transformation to positronic system, we have included backflow displacements which consist of electron–positron two-body ($\xi_i^{\mathrm{e-p}}$) and electron–positron–nucleus three-body terms ($\xi_i^{\mathrm{e-p-n}}$). The total backflow displacement is, therefore, $\xi_i = \xi_i^{\mathrm{e-e}} + \xi_i^{\mathrm{e-n}} + \xi_i^{\mathrm{e-e-n}} + \xi_i^{\mathrm{e-p}} + \xi_i^{\mathrm{e-p-n}}$, where each backflow displacement is expanded as a polynomial in the particle separations. The variational parameters in the Jastrow factor and backflow displacement are optimized using a variational Monte Carlo (VMC) energy minimization scheme.[12] We have used the *CASINO* code[13] for all of the QMC calculations reported here.

The two-photon annihilation rate (Γ_2) was evaluated by the general formula[14] of $\Gamma_2 = \pi\alpha^4 c a_0{}^{-1}\,\langle\delta\rangle$, where $\langle\delta\rangle$ is the expectation value of the electron–positron δ function,

Table 1. Total energy (E_{Tot}), binding energy of positronium (BE, defined as $E_{\mathrm{Tot}}(\mathrm{H}) + E_{\mathrm{Tot}}(\mathrm{Ps}) - E_{\mathrm{Tot}}[\mathrm{H}^-;\mathrm{e}^+]$), and two-photon annihilation rate (Γ_2) for the ground state of the $[\mathrm{H}^-;\mathrm{e}^+]$ system from various methods

Method	E_{Tot}/au	BE/eV	$\Gamma_2/10^9\,\mathrm{s}^{-1}$
HF	−0.66695	−2.260	0.297(3)[a]
VMC (SJ)	−0.78352(4)	0.909(2)	2.32(5)
VMC (SJB)	−0.78675(6)	1.000(2)	2.46(5)
ECG-SVM[b]	−0.789196	1.067	2.471

[a]VMC calculation with Hartree–Fock wave function. [b]Reference 4.

$$\langle\delta\rangle = \sum_i^N \langle\Psi|\delta(\mathbf{r}_i - \mathbf{r}_\mathrm{p})|\Psi\rangle / \langle\Psi|\Psi\rangle \tag{3}$$

and we used the identity $\nabla^2(1/r) = -4\pi\delta(r)$ and integration by parts to obtain an expression for $\langle\delta\rangle$, which is evaluated using VMC.[15]

Table 1 gives the total energy (E_{Tot}), the binding energy of positronium (BE), and the annihilation rate (Γ_2) obtained in a VMC calculation for the ground state of the $[\mathrm{H}^-;\mathrm{e}^+]$ system. The result of the stochastic variational method with an ECG wave function (denoted as "ECG-SVM")[4] is also shown. The VMC calculation with a Slater–Jastrow trial wave function (denoted by "VMC(SJ)") recovers about 95% of the correlation energy, where we assume that the ECG-SVM calculation gives the exact correlation energy. A further reduction in the total energy is achieved by the Slater–Jastrow-backflow (SJB) trial wave function (denoted as "VMC(SJB)"), which gives about 98% of correlation energy. The SJB trial wave function improves not only the total energy but also the BE and Γ_2. The error in the BE is 67(2) meV, and the value of Γ_2 is within statistical error of the exact annihilation rate.

Table 2 shows total energies, positron affinities (PA, which is the binding energy of e^+), and Γ_2 for the ground state of $[\mathrm{Li}^-;\mathrm{e}^+]$. The previous DMC[6,16] and ECG-SVM[17] results are also shown. The SJB trial wave function greatly improves the total energy of $[\mathrm{Li}^-;\mathrm{e}^+]$ compared with the results from the SJ trial wave function. About 91% of the correlation energy is recovered by the SJB trial wave function, while only about 74% is recovered with the SJ trial wave function. The PA and Γ_2 are also improved by the BF transformation. The large differences between the SJ and SJB values of PA and Γ_2 indicate the importance of an accurate description of correlation for evaluating these quantities in positronic compounds. The value of Γ_2 obtained with the SJB trial wave function is within statistical error of the DMC result, and considerably closer to the exact value, even though the total energy is slightly higher than the DMC result and the exact value. Such a remarkable result indicates the advantages of the SJB trial wave function over the SJ one for positronic compounds. It is highly expected that we can obtain even more accurate results by performing a DMC calculation with the Slater–Jastrow-backflow trial wave function.

In this study we have applied an inhomogeneous backflow transformation to Slater–Jastrow trial wave functions for the $[\mathrm{H}^-;\mathrm{e}^+]$ and $[\mathrm{Li}^-;\mathrm{e}^+]$ systems. The backflow transformation greatly improves the properties obtained in variational Monte Carlo calculations. We conclude that the Slater–Jastrow-backflow trial wave function is well suited to studying positronic compounds with quantum Monte Carlo methods.

Table 2. Total energy (E_{Tot}), positron affinity (PA, defined as $E_{\mathrm{Tot}}[\mathrm{Li}^-] - E_{\mathrm{Tot}}[\mathrm{Li}^-;\mathrm{e}^+]$), and two-photon annihilation rate (Γ_2) for the ground state of the $[\mathrm{Li}^-;\mathrm{e}^+]$ system from various methods

Method	E_{Tot}/au	PA/eV	$\Gamma_2/10^9\,\mathrm{s}^{-1}$
HF	−7.52988	2.766	0.06(1)[a]
VMC (SJ)	−7.6871(3)	5.447(15)	1.97(2)
VMC (SJB)	−7.7216(2)	6.208(13)	2.12(2)
DMC	−7.73959(6)[b]	6.506(2)[c]	2.0(1)[b]
ECG-SVM[d]	−7.740208	6.515	2.151

[a]VMC calculation with Hartree–Fock wave function. [b]Reference 16. [c]Reference 6. [d]Reference 17.

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