# Theoretical Study of Positronium Atoms Using Frozen Gaussian-type Geminals

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We report on the theoretical positron affinities of closed-shell atomic anions. The second-order many-body perturbation theory is applied taking the positron-electron interaction as a perturbation. The corrections for the complete basis set effects to the second order affinity are calculated based on the variational and nonvariational energy functionals of explicitly correlated geminals. It is shown that the explicitly correlated methods accelerate the convergence of the expansion significantly giving the account of the cusp behavior outside the orbital space.

**Key Words :** Gaussian-type geminals, Positron affinity, Explicitly correlated MBPT2

## Introduction

Since the existence of positronium (Ps), the simplest pair complex of an electron and a positron, was predicted and discovered.[1,2] various theoretical and experimental studies of positronium complexes have been reported.[3] The self-consistent field (SCF) method has been employed frequently in theoretical treatments.[4] The method is, however, not qualified to give accurate results in many cases due to the absence of the positron-electron correlation effects in the approximation. Diffusion Monte Carlo (DMC) techniques have been rewarded by results in agreement with experiments[5,6] though they are laborious computationally and less suitable for routine calculations. Another way to deal with the positron-electron correlation is to extend methods in molecular orbital theory, as PsOH was calculated at the second-order many-body perturbation theory (MBPT2) level.[7] The orbital expansion requires a large basis set to obtain a saturated result for the cusp behavior between a positron and an electron. (The cusp condition is analogous to the electron correlation[8] but opposite in sign. *i.e.* the slope is −1/2.) For electronic cusps. various alternatives with explicitly correlated functions have been proposed to improve the convergence of a correlated method.[9-13] It is anticipated that such expansions are also effective for describing the binary wave functions of electrons and positrons.

In this paper, we apply SCF and MBPT2 to the positron affinities (PAs) of closed shell anions. MBPT2 corrections are calculated using frozen Gaussian-type geminals for the complete basis effects. It is demonstrated that the results with geminals are improved significantly in convergence compared to the MBPT2 results of orbitals. In what follows, we derive necessary formulae for SCF, MBPT2, and explicitly correlated methods. Results and discussions are presented in Section 3 and conclusions are given in Section 4.

## Theory

Throughout this paper, we use the notations, $i, j, \ldots, a, b,$

... and $p, q$ ... for occupied. virtual and general spin-orbitals, respectively. Positronic orbitals are distinguished by over-bars. as $\bar{i}$. We assume that the systems we are interested in involve only one positron. The SCF method represents the wave function as a product of an electronic determinant and a positron orbital. The SCF energy is given by

$$E = h^p_{\bar{1}\bar{1}} + \sum_i (h^e_{ii} - \langle i\bar{1}|i\bar{1}\rangle) + \frac{1}{2}\sum_{ij}(\langle ij|ij\rangle - \langle ij|ji\rangle). \quad (1)$$

where $\langle pq|rs\rangle$ and $\langle p\bar{q}|r\bar{s}\rangle$ are electron-electron and electron-positron repulsion integrals. $\mathbf{h}^p$ and $\mathbf{h}^e$ are one-body Hamiltonian matrices for the positron and electrons (differing just in the signs of the interactions with nuclei). and $\bar{1}$ denotes the positronic occupied orbital. Minimizing the energy expression with respect to the orbitals, we obtain the SCF equations.

$$f^e_{pi} = \varepsilon^e_i \delta_{pi}, \quad \forall p, i, \quad (2)$$

$$f^p_{\bar{p}\bar{1}} = \varepsilon^e_{\bar{1}} \delta_{\bar{p}\bar{1}}. \quad \forall \bar{p}. \quad (3)$$

which are coupled to each other through the positron-electron interactions in the Fock operators,

$$f^e_{pq} = h^e_{pq} + \sum_i (\langle pi|qi\rangle - \langle pi|iq\rangle) - \langle p\bar{1}|q\bar{1}\rangle. \quad (4)$$

$$f^e_{\bar{p}\bar{q}} = h^e_{\bar{p}\bar{q}} - \sum_i \langle i\bar{p}|i\bar{q}\rangle. \quad (5)$$

The coupled equations are solved iteratively during the SCF cycle.

The positron-electron correlations are dealt with at MBPT2 with the partitioning,

$$H = H_0 + \lambda^{pe} V + \lambda^{ee} W. \quad (6)$$

where the operators, $V$ and $W$, are positron-electron and electron-electron interactions. $\lambda^{pe}$ and $\lambda^{ee}$ are the corresponding charging parameters. and $H_0$ is the SCF model Hamiltonian. *i.e.* the sum of the Fock operators. At the MBPT2 level. $W$ is considered to be much less important than $V$ for PAs because of the cancellation between the states with and without the positron. Thus we use the MBPT2

expression,

$$E^{(2)} = \sum_{ia\bar{a}} \frac{|\langle i\bar{1}|a\bar{a}\rangle|^2}{\varepsilon_i + \varepsilon_{\bar{1}} - \varepsilon_a - \varepsilon_{\bar{a}}}. \tag{7}$$

taking $V$ as a perturbation.

To improve the result with a basis set truncation error in the MBPT2 calculation, we represent the first order wave operator as a sum of a geminal operator and its complement in the usual particle-hole excitation form,

$$\Omega^{(1)} = F_N + T^{(1)}. \tag{8}$$

The vacuum amplitude is set zero,

$$F_N = F - \langle \phi|F|\phi\rangle. \tag{9}$$

in $F_N$ with $F$ which is a sum of spherically symmetric geminals dependent on the positron-electron distance,

$$F = \sum_n^N f(r_{n\bar{1}}). \tag{10}$$

for the number of electrons, $N$. Assuming that the SCF orbitals are exact in the complete basis limit and the commutator between the exchange and the geminal operators are negligible,[10,11] the Rayleigh-Schrödinger condition for the first order wave operator outside the Hilbert space spanned by the orbitals becomes in the form,

$$(Q_1^* \bar{Q}_{\bar{1}}^* - Q_1 \bar{Q}_{\bar{1}})(K_{1\bar{1}}^{(L)} - r_{1\bar{1}}^{-1})|i\bar{i}\rangle = 0, \quad \forall i\bar{i}, \tag{11}$$

where $Q_1^*$ and $Q_1$ are one-electron projectors in the virtual spaces of the complete and given basis sets, respectively, and $\bar{Q}_{\bar{1}}^*$ and $\bar{Q}_{\bar{1}}$ are those for positrons. The operator, $K_{1\bar{1}}^{(L)}$, is an anti-hermite single commutator between the kinetic energy and geminal operators.[13]

$$K_{1\bar{1}}^{(L)} = -\nabla_1^2 f_{1\bar{1}} - \nabla_1 f_{1\bar{1}} \cdot (\nabla_1 - \nabla_{\bar{1}}). \tag{12}$$

The above condition is fulfilled asymptotically for a geminal, $f(r_{1\bar{1}}) = f(0) - (r_{1\bar{1}}/2) + O(r_{1\bar{1}}^2)$, since the convergence of the expansion with orbital products is slow around $r_{1\bar{1}} = 0$. Then we obtain the nonvariational energy functional from the Rayleigh-Schrödinger expansion,

$$E_N^{(2)} = E^{(2)} + \Delta E_N^{(2)}. \tag{13}$$

$$\Delta E_N^{(2)} = \sum_{i\bar{i}} \langle i\bar{i} | K_{1\bar{1}}^{(L)}(Q_1^* \bar{Q}_{\bar{1}}^* - Q_1 \bar{Q}_{\bar{1}}) f_{1\bar{1}} | i\bar{i}\rangle. \tag{14}$$

It is important to compare the expression with the Hylleraas functional.

$$E_V^{(2)} = E^{(2)} - \Delta E_N^{(2)} + 2\Delta E_Z^{(2)}, \tag{15}$$

$$\Delta E_Z^{(2)} = -\sum_{i\bar{i}} \langle i\bar{i} | K_{1\bar{1}}^{-1}(Q_1^* \bar{Q}_{\bar{1}}^* - Q_1 \bar{Q}_{\bar{1}}) f_{1\bar{1}} | i\bar{i}\rangle. \tag{16}$$

All three energy corrections become identical, $\Delta E_V^{(2)} = \Delta E_N^{(2)} = \Delta E_Z^{(2)}$, when the geminal is exact outside the orbital space satisfying Eqn. (11). Hence the ratio,

$$\chi = \Delta E_Z^{(2)} / \Delta E_N^{(2)}, \tag{17}$$

which is unity in the above condition, is a measure to indicate the appropriateness of geminals. Replacing the geminal operator by $\chi F_N$, we obtain the energy expression,

$$E_\chi^{(2)} = E^{(2)} + \chi^2 \Delta E_N^{(2)} = E^{(2)} + \chi \Delta E_Z^{(2)}. \tag{18}$$

which is stationary with respect to $\chi$. One can think of the connection between $\Delta E_N^{(2)}$ and $\Delta E_Z^{(2)}$ as the virial theorem for the cusp condition since they are corrections for the kinetic and potential energy operators, respectively. $\Delta E_N^{(2)}$ is directly obtained from the order-by-order expansion of the Schrödinger equation for the transcorrelated Hamiltonian. In such a way, the first order cusp condition is renormalized to infinite order in the transcorrelated method.

Introducing the one-electron projectors for occupied orbitals, $P_1 = 1 - Q_1^*$ and $\bar{P}_{\bar{1}} = 1 - \bar{Q}_{\bar{1}}^*$, the components in the functional are divided as

$$\Delta E_N^{(2)} = \Delta E_N^{(2)}[1] - \Delta E_N^{(2)}[P_1 + \bar{P}_{\bar{1}}] \\ + \Delta E_N^{(2)}[P_1 \bar{P}_{\bar{1}}] - \Delta E_N^{(2)}[Q_1 \bar{Q}_{\bar{1}}]. \tag{19}$$

$$\Delta E_N^{(2)}[O] = \sum_{i\bar{i}} \langle i\bar{i} | K_{1\bar{1}}^{(L)} O f_{1\bar{1}} | i\bar{i}\rangle. \tag{20}$$

and similar expressions for $\Delta E_Z^{(2)}$. The component, $\Delta E_N^{(2)}[1]$, can be rewritten in the commutator form leading to the operator, $K_{1\bar{1}}^{(Q)}$, which also appears in the transcorrelated method.[13]

$$\Delta E_N^{(2)}[1] = \sum_{i\bar{i}} \langle i\bar{i} | K_{1\bar{1}}^{(Q)} | i\bar{i}\rangle. \tag{21}$$

$$K_{1\bar{1}}^{(Q)} = \frac{1}{2}[K_{1\bar{1}}^{(L)}, f_{1\bar{1}}] = -(\nabla_1 f_{1\bar{1}}) \cdot (\nabla_1 f_{1\bar{1}}). \tag{22}$$

The term with single projectors reduces to 3-electron integrals and is approximated using the resolution of identity (RI) of Kutzelnigg and Klopper[11] as,

$$\langle i\bar{i} | K_{1\bar{1}}^{(L)} P_1 f_{1\bar{1}} | i\bar{i}\rangle \cong \sum_{j\bar{p}} \langle i\bar{i} | K_{1\bar{1}}^{(L)} | j\bar{p}\rangle \langle j\bar{p} | f_{1\bar{1}} | i\bar{i}\rangle. \tag{23}$$

Since the integrals in RI involve three occupied orbitals, the maximum angular momenta required for saturated completeness insertions are $2L_{OCC} + \bar{L}_{OCC}$ and $L_{OCC} + 2\bar{L}_{OCC}$ for the highest occupied ones of the electrons, $L_{OCC}$, and the positron, $\bar{L}_{OCC}$, in an atomic calculation. This fact prohibits the application of RI to a system with heavy atomic elements as involving $d$-occupied orbitals. Most recently, a novel decomposition scheme has been developed using density fitting,[14] which reduces the required maximum angular momentum to $2L_{OCC}$ from $3L_{OCC}$ in the original RI for a pure electron problem. The scheme is not employed in this work as we focus on the positron affinity of light atomic anions.

## Results and Discussions

We calculate $X^-$ and PsX (X = H and F) at SCF and

MBPT2. The orbital centers of positronic and electronic basis sets are fixed at the nuclear position. PAs are calculated taking the energy differences between $X^-$ and PsX. We transform the template geminal for electron-electron correlations[12] with the parameter. $c_z$.

$$f(r_{1\bar{1}};c_z) = c_z^{-1} f'(c_z r_{1\bar{1}}). \tag{24}$$

and change the signs of the coefficients for the treatment of electron-positron correlations. Throughout this work, we use $c_z = 0.45$, which leads to a long-ranged geminal compared to those for electron correlations. For electronic wavefunctions, we use the (7s4p3d2f) and (13s7p4d3f2g) primitives in the aug-cc-pVQZ basis sets[15] for H and F as Cartesian Gaussian-type functions. For positronic wavefunctions, systematic basis sets have not been developed. The SCF orbital of the positron is s-type and spreads because of the large distribution of the electrons in $X^-$. Thus we use slightly large (10s5p4d3f2g) primitives in the aug-cc-pV5Z set augmented by an additional diffuse s-primitive with the exponent, 0.005, both for PsH and PsF. We also inspect the convergence of the positron-electron correlation by increasing the maximum angular momentum.

The probability densities of a positron and an electron in the SCF wave function of PsH are shown in Figure 1. The positronic orbital is more diffuse than those of electrons: the electrons are strongly bound around the nucleus and the positron is weakly captured by the electrostatic field. We tabulate the convergence of the total energy of PsH in Table 1. The asymptotic limit of the second order energy with the present partitioning is *ca.* -38.5 mEh. The slightly positive increments of $E_{\Gamma}^{(2)}$ and $E_{\chi}^{(2)}$ from (7s4p3d/10s5p4d) to (7s4p3d2f/10s5p4d3f) are due to the neglect of the
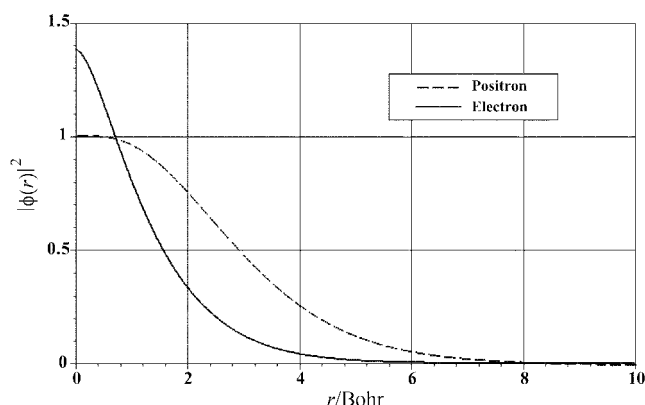
commutator between the exchange and geminal operators. The calculation with the (7s/10s) set reproduces just 17% (-6.4 mEh) of the limit in the MBPT2 without corrections. The error is substantially reduced by the introduction of the explicitly correlated geminal to recover *ca.* 87% (-33.5 mEh) of the correlation energy in $E_{\chi}^{(2)}$. The results of PAs are summarized in Table 2 and Figure 2. Schrader and coworkers succeeded in the formation of PsH applying the positron beam with different momenta to the methane molecule.[5] Experimentally, the binding energy between Ps and the hydrogen atom is estimated to be $1.1 \pm 0.2$ eV. Using the energy of Ps. 6.8 eV. and the electron affinity of Hydrogen. 0.8 eV. the experimental positron affinity is derived to be $7.1 \pm 0.2$ eV. The present estimate of the PA in the MBPT2 limit is 5.92 eV which deviates from the experiment by 1.2 eV. From the small error bar in the experimental PA. the main source of the deviation is considered to be the absence of the third and higher order contributions in the present theoretical treatment. The affinities of the second order energies with the geminal corrections almost saturates at the calculation with the
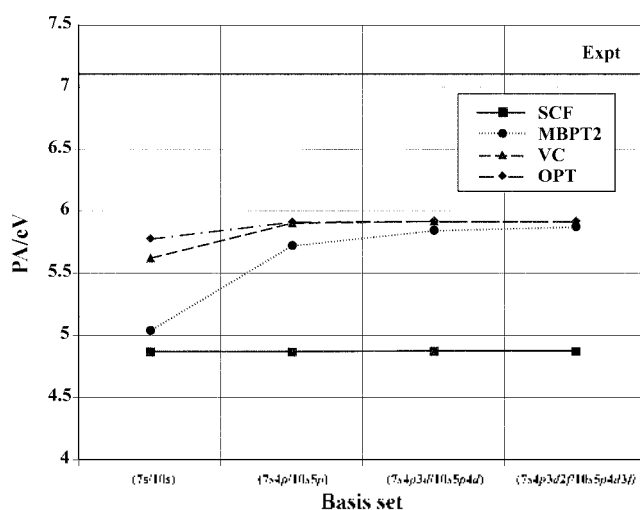
**Table 2.** PA[a] of $H^-$ (in eV)

| Basis | (Electron/Positron) | SCF | MBPT2 | VC | OPT | EXP[b] |
|-------|---------------------|------|-------|------|------|--------|
| 1 | (7s/10s) | 4.86 | 5.04 | 5.62 | 5.78 | 7.10 |
| 2 | (7s4p/10s5p) | 4.86 | 5.72 | 5.90 | 5.91 | |
| 3 | (7s4p3d/10s5p4d) | 4.87 | 5.84 | 5.92 | 5.92 | |
| 4 | (7s4p3d2f/10s5p4d3f) | 4.87 | 5.87 | 5.92 | 5.92 | |

[a]VC. and OPT mean the PAs calculated from $E_{\Gamma}^{(2)}$. and $E_{\chi}^{(2)}$, respectively.
[b]Reference 5.



**Figure 1.** Probability densities of a positron and an electron in the SCF wave function of PsH.



**Figure 2.** Theoretical and experimental PAs of $H^-$ in eV.

**Table 1.** Energy components of PsH and $H^-$ (in mEh)

| Basis | (Electron/Positron) | $E_{SCF}$(PsH) | $E^{(2)}$ | $E_N^{(2)}$ | $E_{\Gamma}^{(2)}$ | $E_{\chi}^{(2)}$ | $\chi$ | $E_{SCF}$($H^-$) |
|-------|---------------------|----------------|-----------|-------------|---------------------|-------------------|--------|-------------------|
| 1 | (7s/10s) | -666.54 | -6.38 | -14.39 | -27.86 | -33.54 | 1.84 | -487.81 |
| 2 | (7s4p/10s5p) | -666.54 | -31.48 | -35.91 | -38.18 | -38.47 | 1.26 | -487.81 |
| 3 | (7s4p3d/10s5p4d) | -666.76 | -35.76 | -38.29 | -38.57 | -38.58 | 1.06 | -487.83 |
| 4 | (7s4p3d2f/10s5p4d3f) | -666.76 | -36.88 | -38.50 | -38.50 | -38.50 | 1.00 | -487.83 |

**Table 3.** Energy components of PsF and F⁻ (in mEh)

| Basis | (Electron/Positron) | $E_{SCF}$(PsF) | $E^{(2)}$ | $E_N^{(2)}$ | $E_F^{(2)}$ | $E_\chi^{(2)}$ | $\chi$ | $E_{SCF}$(F⁻) |
|---|---|---|---|---|---|---|---|---|
| 1 | (13s7p/10s5p) | -99641.13 | -6.44 | -26.79 | -29.36 | -29.44 | 1.06 | -99457.46 |
| 2 | (13s7p4d/10s5p4d) | -99641.34 | -23.14 | -31.15 | -28.57 | -28.78 | 0.84 | -99457.51 |
| 3 | (13s7p4d3f/10s5p4d3f) | -99641.48 | -26.37 | -30.11 | -28.58 | -28.74 | 0.80 | -99457.71 |
| 4 | (13s7p4d3f2g/10s5p4d3f2g) | -99641.50 | -27.25 | -29.31 | -28.65 | -28.70 | 0.85 | -99457.71 |

**Table 4.** PA of F⁻ (in eV)

| Number | (Electron/Positron) | SCF | MBPT2 | VC | OPT | DMC[a] | EXP[b] |
|---|---|---|---|---|---|---|---|
| 1 | (13s7p/10s5p) | 5.00 | 5.17 | 5.80 | 5.80 | 6.17 | 6.30 |
| 2 | (13s7p4d/10s5p4d) | 5.00 | 5.63 | 5.78 | 5.79 | | |
| 3 | (13s7p4d3f/10s5p4d3f) | 5.00 | 5.72 | 5.78 | 5.78 | | |
| 4 | (13s7p4d3f2g/10s5p4d3f2g) | 5.00 | 5.74 | 5.78 | 5.78 | | |

[a]Reference 6. [b]Reference 16.

(7s4p3d/10s5p4d) set to converge much faster than the conventional MBPT2.

We show the energy components of PsF and F⁻ in Table 3. In the result with the (13s7p/10s5p) set, the conventional MBPT2 reproduces only 23% of the asymptotic limit of the second order energy, ca. -29 mEh. The results with the variational corrections are almost saturated with the basis sets involving d-shells. $E_F^{(2)}$ with the (13s7p/10s5p) set is lower than the limit by 0.3 mEh mainly due to the unsaturated RI with the basis set. The saturated RI requires d- and p-functions in the electronic and positronic basis, respectively. We show the theoretical and experimental PAs in Table 4 and Figure 3. The experimental value is derived from the binding energy of PsF, 2.9 ± 0.5 eV, reported by Tao and Green[16] by adding the electron affinity of the Fluorine atom, 3.4 eV. The result from the diffusion Monte Carlo simulation (DMC) is 6.2 eV.[6] The best result in the present calculation, 5.8 eV, is slightly smaller than the PAs of the experiment and DMC by 0.5 and 0.4 eV, respectively.

To summarize, 79% and 92% of the experimental PA of PsF are reproduced at SCF and MBPT2, respectively. This is in contrast with the ratios, 68% and 83%, for PsH. The

difficulty in the treatment of PsH is partly implied by the restricted HF energy of H⁻, -488 mEh, which is higher than the hydrogen energy, -500 mEh. The reference function for the MBPT2 is thus an artifact due to the spin restriction, and the state of H⁻ does not become bound until the electron correlation is treated appropriately.[11a] It is thus concluded that the inclusion of higher order perturbations involving electron-electron interaction is crucial for an accurate PA of PsH.

## Conclusion

We applied the SCF and MBPT2 methods to the calculations of positronic compounds. It has been demonstrated that the positron-electron correlation is essential for quantitative PAs in the results of MBPT2. It was also shown that the variational and nonvariational MBPT2 correction of the explicitly correlated geminal accelerates the convergence of the expansion. Such an application will enable us to calculate PAs of large molecules, to which the access with an enormous basis set is difficult.

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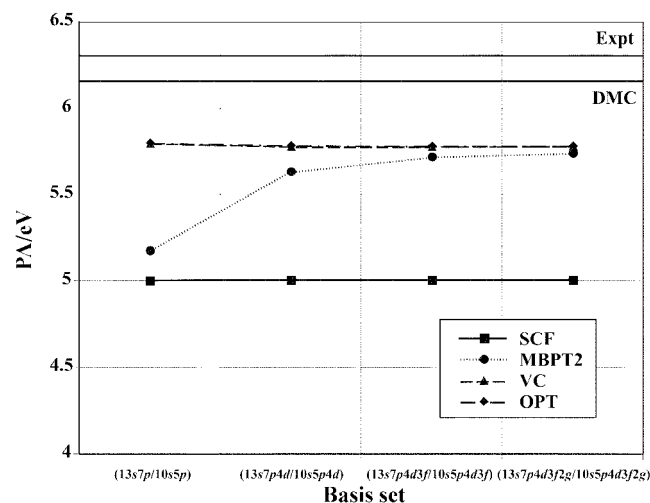
**Figure 3.** Theoretical and experimental PAs of F⁻ in eV.

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