

Binding Energy of Positronium Chloride: A Quantum Monte Carlo Calculation

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The binding energy of positronium chloride is calculated using a model potential for the ten core electrons and the quantum Monte Carlo method for the eight valence electrons and the positron. The result is 1.91 ± 0.16 eV. Except for three- and four-particle systems, this is the first accurate calculation of the binding energy of a compound containing a positron.

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Compounds containing a positron in addition to electrons and nuclei are important in several areas: surface studies, ceramic and doped C_{60} superconductors, radiation chemistry, many-body quantum mechanics, voids in polymers and molecular crystals, mass spectrometry (especially of biologically significant compounds), etc. [1]. In spite of their importance, our knowledge of their binding energies is extremely sparse. No direct measurements have been reported, although very recent progress has been made [2]. Except for the present work, accurate quantum mechanical calculations have been applied only to two-, three-, and four-particle systems.

Positronium chloride (PsCl) is an atom consisting of a chlorine atom combined with a positronium atom. It is stable compared to separated Cl and Ps atoms. Its ACAR (angular correlation of annihilation radiation) spectrum has been observed in aqueous solutions of chloride ions [3–5], graphite-intercalated chloride compounds [6,7], and chloride-doped polyacetylene [8]. The observed ACAR curves agree closely with that calculated from the Hartree-Fock wave function for gaseous PsCl [9] (although adding waters of hydration to the calculation degrades the agreement somewhat [10]). None of this experimental work gives an indication of the magnitude of the binding energy—just its sign. An assertion has been made that the PAL (positron annihilation lifetime) spectrum of chlorine gas and of argon-chlorine gas mixtures gives the Ps-Cl bond strength as 2.0 ± 0.5 eV [11]. Experimental evidence supporting this assertion was not given [11,12].

Theoretical evidence that PsCl is bound was provided in 1953 by Simons, who calculated a positronic orbital in the fixed field of a chloride ion represented by a Hartree-Fock wave function [13]. Simons' calculated Ps-Cl bond energy was 0.59 eV, which is a lower bound. This calculation was repeated some years later with a more modern chloride wave function, with similar results [14]. Cade and Farazdel added full self-consistency, which increased the calculated bond energy slightly to 0.73 eV [15,16]. These calculations omit two important sources of stability for the system: polarization and correlation. The first is a

long-range effect and can be adequately treated in a very simple way by including a polarization potential term in the Hartree-Fock equation for the positron.

Correlation is a short-range effect and is much more difficult to treat by conventional quantum mechanical techniques. The purely electronic correlation energy amounts to about 20 eV [17]. The PsCl binding energies quoted in this paragraph are compromised because they rest on the assumption that the electronic correlation energy in Cl^- is the same as in PsCl.

The polarization effect in PsCl has been treated in several one-particle model potential calculations to various degrees of accuracy [18–21]. The most recent of these calculations gives a binding energy of 1.40 eV [21]. However, the model potential for Cl^- is parametrized by calculations on three small systems: (e^+, H) and (e^+, He) , both unbound, and PsH, which is bound. It is not clear that these small systems serve as a reliable guide to the properties of a many-particle system such as PsCl.

Correlation and the quantum Monte Carlo method.—The crucial role of electron-positron correlation in calculating energies and annihilation rates has been stressed [22]. Calculations using wave mechanics and the Ritz variational principle are exceedingly difficult owing to integral evaluations, and to date have been carried out with good accuracy only for the three-body systems PsH [23] and Ps_2 [24]. The quantum Monte Carlo (QMC) method is comparatively very easy to use, and gives an accuracy limited only by computer time.

We choose a method which combines a model potential (MP) for the *K*- and *L*-shell electrons and the QMC method, a procedure we designate as MP-QMC. This method recently yielded the electron affinity of Cl as 3.617 ± 0.198 eV [25], compared to the experimental value of 3.615 eV. An added positron probes the outer regions of Cl^- , so inaccuracies in the core potential are less important. Therefore, MP-QMC yields a reliable energy for the system PsCl, from which the bond energy is obtained with much greater accuracy and rigor than is given by any previous work. This is the subject of the present Letter.

TABLE I. Parameters in Eq. (2).

k	μ_k	B_k	β_k
1	0	1.428 57	5.896 50
2	5	39 751.4	27
3	5	-10.8414	8

Accommodating the positron.—The procedure used here is the same as for Cl and Cl⁻ previously reported, [25] and is not repeated. Instead, we describe only the changes made to add a positron to Cl⁻.

We take the Hamiltonian for PsCl to be

$$H = \sum_{i=1}^{N_e} \left\{ -D\nabla_i^2 + V_{\text{MP}}(i) + \sum_{j>i}^{N_e} \frac{e^2}{r_{ij}} \right\} - D\nabla_p^2 + V_{\text{MP}}^{(+)}(p) - \sum_{i=1}^{N_e} \frac{e^2}{r_{ip}}, \quad (1)$$

where N_e is the number of valence electrons (i.e., the eight 3s and 3p electrons), D is the diffusion coefficient $\hbar^2/2m_e$, and $V_{\text{MP}}(i)$ and $V_{\text{MP}}^{(+)}(p)$ are model potentials for the i th electron and the positron, respectively, interacting with the ten core electrons. $V_{\text{MP}}(i)$ is the same as used previously. $V_{\text{MP}}^{(+)}(p)$ is taken to be

$$V_{\text{MP}}^{(+)}(p) = \frac{Z - N_c}{r_p} \left\{ 1 + \sum_{k=1}^K B_k r_p^{\mu_k} e^{-\beta_k r_p} \right\}, \quad (2)$$

where N_c is the number of core electrons (ten in this case). The parameters B_k , μ_k , and β_k are obtained by fitting the expression on the right above with

$$\frac{Z}{r_p} - 2 \sum_{j \text{ in core}}^{N_c/2} J_j(\mathbf{r}_p),$$

by a least-squares minimization procedure. $J_j(\mathbf{r})$ is the Coulomb potential at \mathbf{r} generated by the j th core orbital, which are given by Clementi and Roetti [26]. A fit within the width of a line on a plot of the two functions is achieved for the number of terms K equal to 3. The values of the parameters are given in Table I.

The importance function is taken to be of the form [22]

$$\begin{aligned} \Psi_T &= \varphi_p(r_p) \alpha(p) \mathcal{A} \prod_{i=1}^{N_e} \varphi_i(\mathbf{r}_i, r_{ip}) \sigma(i), \\ \varphi_i(\mathbf{r}_i, r_{ip}) &= \varphi_i^{\text{HF}}(\mathbf{r}_i) e^{-r_{ip}/2}, \\ \sigma(i) &= \begin{cases} \alpha(i) & \text{for } i \text{ odd,} \\ \beta(i) & \text{for } i \text{ even.} \end{cases} \end{aligned} \quad (3)$$

φ_i^{HF} are Hartree-Fock orbitals for the 3s and 3p electrons of Cl⁻ [26], α and β are the usual spin functions, \mathcal{A} orthogonalizes and normalizes, and φ_p , the positron orbital, is either $r^2 e^{-ar}$ or $r^3 e^{-ar}$ (normalized) with a being determined by fitting $\langle r^n \rangle$ averaged over φ_p for $n = -1, 1, 2$ to values given by Farazdel [27]. These two choices for φ_p gave almost identical results for the Ps-Cl bond energy. For the first choice above, $a = 0.66$.

TABLE II. Valence energies of Cl and PsCl vs time steps. Statistical uncertainties are indicated in parentheses. All numbers are in atomic units.

Time step	Cl ^a	PsCl
0.01	-14.924 80(316)	-15.187 09(459)
0.005	-14.912 22(402)	-15.208 24(462)
0.0025	-14.912 42(342)	-15.218 82(463)
0.001 25	-14.910 97(342)	
0.0 ^b	-14.908 86(349)	-15.229 40(465)

^aFrom Ref. [25].

^bExtrapolated.

Ψ_T above does not include the core electrons, but otherwise it has correct cusp values for the attractive particle pairs, and therefore is a good representation of the probability density in important regions of space.

Valence energies of Cl and PsCl for different time steps are given in Table II. These are extrapolated to zero time by a linear weighted least-squares fit. The weighting factor for each point is $1/\delta t (\delta E)^2$, δt , and δE being the time step and statistical uncertainty in the energy, respectively. The difference of the extrapolated energies less 6.8 eV, the binding energy of Ps, is the bond strength of PsCl. We find this quantity to be 1.92 ± 0.16 eV. This is in fairly good agreement with the most recent model potential result, 1.40 eV [21], and in excellent agreement with the older estimate from the annihilation rates of positrons in Cl₂ and Ar-Cl₂ gases [11]. The latter agreement is probably fortuitous.

The uncertainty in our result, 0.16 eV, reflects the statistical fluctuations inherent in the QMC method. There may be small systematic errors common to all the energies given in Table II arising from errors in the model potential, nodes of the importance function, etc.

In view of the absence of rigorous previous work, either experimental or theoretical, we believe our result is much more reliable than any other reported to date.

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