

van der Waals Force Between Positronium and Hydrogenic Atoms: Finite-Mass Corrections

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The Feshbach projection-operator formalism is used to derive the asymptotic effective interaction potential between two atoms. Beyond the usual van der Waals potential, falling like x^{-6} , three x^{-8} terms are also obtained: an attractive dipole-quadrupole term (absent in the positronium-positronium case because of symmetry), a repulsive energy-dependent term, and a repulsive mass-dependent but energy-independent one. This last term was not obtained by Manson and Ritchie using an independent method.

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Systems containing positronium (Ps) atoms are of increasing interest, partly because of modern experimental techniques,¹ but there are questions of theoretical interest as well.² Some time ago Martin and Fraser³ made accurate computations of the van der Waals coefficients (C_6) for Ps-Ps, Ps-H, and Ps-He systems, for use in future scattering calculations. More recently, Manson and Ritchie⁴ pointed out that the Born-Oppenheimer approximation, used for ordinary diatomic systems, is inappropriate for objects as light as Ps. They used a certain "completely quantal" technique and obtained corrections due to recoil. In this Letter we apply a different technique^{5,6} that has been very successful in describing the polarization forces acting between electrons and atoms, and we derive finite-mass corrections different from those of Ref. 4.

We consider the scattering at low energy of a Ps atom by another hydrogenic atom consisting of an electron and some singly charged positive particle of mass M . (This is not the most general possible case, but it does include Ps, hydrogen, and muonium.) In Rydberg units the Hamiltonian is

$$H = -\frac{1}{M} \nabla_{+1}^2 - \nabla_{+2}^2 - \nabla_{-1}^2 - \nabla_{-2}^2 + \frac{2}{|\mathbf{r}_{+1} - \mathbf{r}_{+2}|} + \frac{2}{|\mathbf{r}_{-1} - \mathbf{r}_{-2}|} - \sum_{i,j=1}^2 \frac{2}{|\mathbf{r}_i - \mathbf{r}_j|}. \quad (1)$$

Since we are interested in long-range forces, we can assume that the otherwise identical particles are distinguishable, and since all the particles have finite masses it is important to measure the positions of the two atoms from their centers of mass. This is accomplished by transformation to the following Jacobi coordinates:

$$\mathbf{R} = \frac{M\mathbf{r}_{+1} + \mathbf{r}_{+2} + \mathbf{r}_{-1} + \mathbf{r}_{-2}}{M+3}, \quad \mathbf{x} = \frac{\mathbf{r}_{+2} + \mathbf{r}_{-2}}{2} - \frac{M\mathbf{r}_{+1} + \mathbf{r}_{-1}}{M+1}, \quad \boldsymbol{\rho}_1 = \mathbf{r}_{-1} - \mathbf{r}_{+1}, \quad \boldsymbol{\rho}_2 = \mathbf{r}_{-2} - \mathbf{r}_{+2}. \quad (2)$$

Here \mathbf{R} is the center of mass of the whole system, and \mathbf{x} is the vector joining the centers of mass of the two atoms. It is our objective to derive an effective Schrödinger equation in the coordinate \mathbf{x} to describe the scattering.

In these transformed coordinates the Hamiltonian takes the form

$$H = H_0 + T + V, \quad \text{where } H_0 = -\left(1 + \frac{1}{M}\right) \nabla_1^2 - \frac{2}{\rho_1} - 2\nabla_2^2 - \frac{2}{\rho_2} \quad \text{and } T = -\left(\frac{3+M}{2[1+M]}\right) \nabla_{\mathbf{x}}^2. \quad (3)$$

(We have omitted the kinetic energy of the total center of mass which can be set equal to zero.) The interatomic potential energy is

$$V = 2 \sum_{i=1}^2 (-1)^i \left\{ \left| \mathbf{x} - \frac{M}{1+M} \boldsymbol{\rho}_1 + \frac{1}{2} (-1)^i \boldsymbol{\rho}_2 \right|^{-1} - \left| \mathbf{x} + \frac{1}{1+M} \boldsymbol{\rho}_1 + \frac{1}{2} (-1)^i \boldsymbol{\rho}_2 \right|^{-1} \right\}. \quad (4)$$

The familiar Feshbach method⁵ begins with the definition of an open-channel projection operator $P = P^2$ that has the property that $P\Psi = \Psi$ for large values of the interatomic distance x ; here Ψ is the total scattering wave function corresponding to some incident energy E in the center-of-mass system. These conditions are not sufficient to determine P , but the requirement that all the virtual excitations of the two atomic systems should be in the

closed-channel subspace projected by $Q = 1 - P$ leads to the direct product form

$$P = P_1 \times P_2, \text{ where } P_i = |1s_i\rangle\langle 1s_i|. \quad (5)$$

In the usual way⁶ this leads to a Schrödinger equation of the form

$$P(H - E)P|\Psi\rangle + PVQ\frac{1}{Q(E - H)Q}QVP|\Psi\rangle = 0. \quad (6)$$

This is formally the desired equation, since it lies entirely in the P space, while the effect of all virtual excitations is in the second, optical-potential term. Finally, we can define an effective one-body scattering function that describes the relative motion of the two atoms, $F(\mathbf{x}) = \langle 0|\Psi\rangle$, where the symbol $\langle 0| = \langle 1s_1 1s_2|$ refers to the combined ground states of both atoms, and we can rewrite the scattering equation in the form

$$-\mu^{-1}(\nabla_x^2 + k^2)F(\mathbf{x}) + U(x)F(\mathbf{x}) = 0, \text{ with } \mu = 2(1 + M)/(3 + M). \quad (7)$$

Here the optical potential U is simply related to the second term in Eq. (6) and \mathbf{k} is the momentum in the center-of-mass system. To evaluate the optical potential in the asymptotic region, we will carry out a binomial expansion of its denominator.⁶ Let us make the following definitions:

$$Q(E - H)Q = d - h - QVQ, \text{ where } d = Q(E_0 - H_0)Q, \text{ and } h = -\mu^{-1}Q(\nabla_x^2 + k^2)Q. \quad (8)$$

If we assume for the moment that d , representing the spectrum of the two atoms, is greater than the other terms in Eq. (8), which are the recoil and Coulomb perturbations, respectively, we can write

$$\frac{1}{Q(E - H)Q} \approx \sum_{j=1} \frac{h^{j-1}}{d^j} + \frac{1}{d}QVQ\frac{1}{d} + \dots \quad (9)$$

We will see shortly that the leading term in V for large values of x decreases like x^{-3} and hence only two factors of V need be retained in our expansion if U is to be correct to order x^{-8} . Therefore the final form of the optical potential is the following:

$$U(x) \approx \sum_{j=1} \langle 0|VQ(h^{j-1}/d_j)QV|0\rangle; \quad (10)$$

this corresponds to the nonretarded two-photon-exchange approximation.⁷

Expanding the potential V [Eq. (4)] for large values of x we obtain the leading (dipole-dipole) term

$$V_{\text{dd}} \sim (2/x^3)[\rho_1 \cdot \rho_2 - 3(\rho_1 \cdot \mathbf{x})(\rho_2 \cdot \mathbf{x})], \quad (11)$$

which is independent of mass, and the next order (quadrupole-dipole) term

$$V_{\text{qd}} \sim \frac{3}{x^4} \left(\frac{1-M}{1+M} \right) [5(\rho_1 \cdot \mathbf{x})^2(\rho_2 \cdot \mathbf{x}) - \rho_1^2(\rho_2 \cdot \mathbf{x}) - 2(\rho_1 \cdot \mathbf{x})(\rho_1 \cdot \rho_2)], \quad (12)$$

which is seen to vanish⁸ when $M = 1$, the Ps-Ps case. We will next evaluate all terms in the optical potential up to order x^{-8} , using these asymptotic forms.

In Eq. (10) the term with $j = 1$ gives the ordinary Born-Oppenheimer parts of $U(x)$, since the mass-dependent recoil effects come from the operator h . To see this, we expand the operator Q in a complete set of eigenfunctions of H_0 :

$$Q = |n_1 n_2\rangle\langle n_1 n_2|, \quad U^1(x) = -\frac{|\langle n_1 n_2|V|0\rangle|^2}{\Delta(n_1 n_2)}, \quad \Delta(n_1 n_2) = E_{n_1} + E_{n_2} - E_0, \quad (13)$$

where summation over all states n_1 and n_2 (except $1s$) is understood. The $j = 1$ part of the optical potential then takes the form

$$U^1(x) = -\frac{C_6}{x^6} - \frac{C_8}{x^8}, \text{ where } C_6 = 24 \frac{|\langle 1s_1|P_1(1)\rho_1|n_1\rangle\langle 1s_2|P_1(2)\rho_2|n_2\rangle|^2}{\Delta(n_1 n_2)} \quad (14)$$

$$\text{and } C_8 = 60 \left(\frac{1-M}{1+M} \right)^2 \frac{|\langle 1s_1|P_2(1)\rho_1^2|n_1\rangle\langle 1s_2|P_1(2)\rho_2|n_2\rangle|^2}{\Delta(n_1 n_2)}.$$

The $j = 2$ term in Eq. (10), including only V_{dd} in the potential, gives the recoil correction of order x^{-8} . To see

that we can write

$$U^2(x) = \frac{f^*(n_1 n_2) h f(n_1 n_2)}{[\Delta(n_1 n_2)]^2}, \text{ where } f(n_1 n_2) = \langle n_1 n_2 | V_{\text{dd}} | 0 \rangle. \quad (15)$$

Since the optical potential is to be used only in the scattering equation (7), we can commute h to the right in Eq. (15) and allow it to operate on $F(\mathbf{x})$. Since the leading term in $U(x)$ goes like x^{-6} , we may set $hF(\mathbf{x}) = 0$ whenever it appears. In addition, $\nabla_x^2 V = 0$ since Laplace's equation holds in the asymptotic region. In this way we obtain the expression

$$U^2(x) = -\frac{1}{\mu} \frac{f^*(n_1 n_2) 2 \nabla_x f(n_1 n_2) \cdot \nabla_x}{[\Delta(n_1 n_2)]^2} = -\frac{1}{\mu} \frac{\nabla_x [f(n_1 n_2)]^2 \cdot \nabla_x}{[\Delta(n_1 n_2)]^2}. \quad (16)$$

The second form of this expression requires only that $f(n_1 n_2)$ be real, and once the summation has been carried out no angular parts remain. Finally,

$$U^2(x) = -\frac{D}{\mu} \nabla_x \left(\frac{1}{x^6} \right) \cdot \nabla_x = \frac{6D}{\mu x^7} \frac{\partial}{\partial x}, \quad (17)$$

where D is obtained from C_6 by squaring of the denominators in Eq. (14). (The inconvenient form of this term will be simplified by a transformation later.)

Finally, we consider the $j = 3$ term in the optical potential. This is

$$U^3(x) = -\frac{f^*(n_1 n_2) h^2 f(n_1 n_2)}{[\Delta(n_1 n_2)]^3} = \frac{2}{\mu^2 \Delta^3} f^*(\partial_\alpha \partial_\beta f) \partial_\alpha \partial_\beta, \quad (18)$$

where summation from 1 to 3 over repeated indices is understood, ∂_α is a rectangular component of ∇_x , and we have suppressed the indices n_i . In Eq. (18) we have again commuted h to the right and assumed that the optical potential acts on a scattering function F . If we write

$$V = (2/x^3) [\rho_{1i} \rho_{2i} - (3/x^2) \rho_{1i} \rho_{2j} x_i x_j], \quad (19)$$

carry out the differentiations indicated in Eq. (18), and recall that $\langle 0 | \rho_{1i} \rho_{2j} | n_1 n_2 \rangle \langle n_1 n_2 | \rho_{1k} \rho_{2m} | 0 \rangle$ vanishes unless $i = k$ and $j = m$, we obtain

$$U^3(x) = \frac{24G}{\mu^2 x^8} \left[\delta_{\alpha\beta} - \frac{3x_\alpha x_\beta}{x^2} \right] \partial_\alpha \partial_\beta = \frac{24G}{\mu^2 x^8} \left[\nabla_x^2 - 3 \frac{\partial^2}{\partial x^2} \right], \quad (20)$$

where the constant G is obtained from C_6 in Eq. (14) by cubing of the denominators. After we relate the second partial derivative to the Laplacian and invoke the equation satisfied by F this yields the final expression

$$U^3(x) = \frac{48G}{\mu^2 x^8} \left[k^2 + \frac{3}{x} \frac{\partial}{\partial x} - \frac{3L[L+1]}{2x^2} \right]. \quad (21)$$

(Only the first term is of the required order.) At this stage our scattering equation has the following appearance:

$$-\frac{1}{\mu} (\nabla^2 + k^2) F(\mathbf{x}) + \left[-\frac{C_6}{x^6} + \frac{6D}{\mu x^7} \frac{\partial}{\partial x} - \frac{C_8}{x^8} + \frac{48Gk^2}{\mu^2 x^8} \right] F(\mathbf{x}) = 0. \quad (22)$$

The derivative term in Eq. (22) can be eliminated by making the transformation⁹ to a new scattering function: $F(\mathbf{x}) = \exp(-D/2x^6) \chi(\mathbf{x})$, where the phase shift is unchanged since $\chi = F$ for large values of x . To order x^{-8} the only effect of this transformation is to modify the derivative term in Eq. (22) which becomes

$$-\frac{1}{\mu} (\nabla^2 + k^2) \chi(\mathbf{x}) - \frac{C_6}{x^6} \chi(\mathbf{x}) + \frac{(-C_8 + 15D/\mu + 48Gk^2/\mu^2)}{x^8} \chi(\mathbf{x}) = 0. \quad (23)$$

Equation (23) is our main result. It displays the ordinary van der Waals potential and the next-order term, both adiabatic terms not involving the reduced mass. The recoil or "first nonadiabatic" term is new; in Ref. 4 it is explicitly stated that no such term should exist, but we seem to have derived it here in a straightforward manner. It is essential in the derivation *not* to replace the gradient operator by the momentum¹⁰ $i\mathbf{k}$, even though ∇^2 can properly be replaced by $-k^2$. The energy-dependent term is similar to one obtained in Ref. 4. We emphasize that no proof of the convergence of this expansion in inverse powers of x exists; it is probably asymptotic and perhaps not

unique.

For these simple hydrogenic atoms it is possible to calculate accurate numerical values for all the constants appearing in the optical potential by adapting a technique used by Martin and Fraser.³ Instead of constructing the operator Q from a complete set of eigenfunctions of H_0 as in Eq. (13), we use some convenient finite set of pseudostates to approximate it. In Ref. 3 p -wave basis functions of the form $Y_1^0(r)r^j \exp(-\alpha r)$ were used to diagonalize H_0 . Since the resulting linear combinations are orthonormal, they and the corresponding expectation values of QH_0Q may be used in place of $|n_1 n_2\rangle$ and $E_{n_1} + E_{n_2}$ in all expressions. In fact, this process converges extremely rapidly; in Ref. 3 only ten terms are needed to evaluate C_6 to ten significant figures. Using energies and matrix elements from Ref. 3 we have computed D and G . The coefficient C_8 involves d states, and we first carried out a straightforward ten-term diagonalization analogous to that in Ref. 3. In addition, we were able to apply a theorem¹¹ that relates higher multipole moments to dipole moments; the coefficient C_8 obtained in this way agreed to seven significant figures with the value obtained directly. The results for Ps-H ($M=1836.15$) are $C_6=69.670175$, $C_8=636.1798$, $D=53.114896$, and $G=41.877568$. For the Ps-Ps case ($M=1$) we get $C_6=415.937709$, $C_8=0$, $D=473.512014$, and $G=557.632617$. Finally,

$$U_{\text{Ps-H}}(x) = -\frac{69.6702}{x^6} + \frac{(503.626k^2 - 237.384)}{x^8}, \quad U_{\text{Ps-Ps}}(x) = -\frac{415.938}{x^6} + \frac{(7102.68 + 26766.4k^2)}{x^8}. \quad (24)$$

It may be interesting to find the range in x over which these asymptotic expansions are valid and useful, where the second term is much smaller than the first. For the Ps-H case $x \gg 1.84$ and for Ps-Ps $x \gg 4.13$ are the ranges of validity at $k^2=0$. Since we have no information about the next term in the expansion, we cannot estimate the magnitude of the error.

This Letter has given an alternative derivation of the leading corrections to the van der Waals interaction between Ps atoms and both Ps and H, which differs from the previously reported form.⁴ We have used a method⁶ that has proven useful in treating the similar corrections which appear in the long-range interaction of electrons and hydrogenic atoms: The Feshbach projection technique enables us to work with scattering states and simplifies the bookkeeping involving virtual excitations. We have also been particularly careful to treat the kinematics of the Ps atoms correctly, by defining the interatomic distance to be between the centers of mass of the two atoms. We would like to encourage further discussion of this interesting topic.

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