

van der Waals coefficients for positronium-atom interactions

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(Received 23 April 2003; published 19 September 2003)

The van der Waals coefficients for positronium interactions with a number of rare gases (He, Ne, Ar, Kr, and Xe) and alkali-metal atoms (Li, Na, K, and Rb) are estimated using a variety of *ab initio* and semiempirical methods. Dispersion coefficients are also presented for atomic hydrogen and a number of rare-gas and alkali-metal atoms for validation purposes.

DOI: 10.1103/PhysRevA.68.035201

PACS number(s): 36.40.-c, 36.10.-k, 31.10.+z, 34.50.-s

I. INTRODUCTION

The description of the physics of positronium (Ps) atom scattering is a topic of considerable complexity due to the fact that the two scattering objects are composite objects with their own internal structure [1]. The Ps-atom interaction for a rare-gas target is known to be repulsive at short distances as the Pauli principle excludes the electron in the incident Ps atom from occupying the lowest-energy electron states. Further away from the atom, the Ps-atom interaction should be attractive due to the van der Waals interaction. This attractive interaction will impact upon the scattering cross section since it provides the leading-order term in the effective range expansion for the $\ell \geq 2$ phase shifts close to threshold.

Although the van der Waals interaction is the predominant factor in determining the near threshold behavior of the higher partial waves, almost nothing is known about the van der Waals coefficients for most Ps-atom systems. For example, the coefficient in the leading $1/R^6$ term of the van der Waals potential, the C_6 parameter is only known for H [2–4] and He [2–4].

In this work, a variety of methods are used to estimate the C_6 parameter of the van der Waals interaction between Ps and a number of atoms. Results are presented for the alkalis and the rare gases.

II. CALCULATIONS AND RESULTS

The leading term in the interaction between two electrically neutral but polarizable systems is

$$V(R) \approx -C_6/R^6 + O(1/R^8), \quad (1)$$

where R is the distance between the respective centers of mass. The effective range expansion for the ℓ th partial wave for the van der Waals interaction [5] is

$$\tan(\delta_\ell) \approx \frac{6C_6\pi k^4}{(2\ell+5)(2\ell+3)(2\ell+1)(2\ell-1)(2\ell-3)} \quad (\ell \geq 2). \quad (2)$$

All the estimates of C_6 were computed using the oscillator strength sum rule,

$$C_6 = \frac{3}{2} \sum_{ij} \frac{f_{0i}f_{0j}}{\epsilon_{0i}\epsilon_{0j}(\epsilon_{0j} + \epsilon_{0i})}. \quad (3)$$

In this expression f_{0i} and f_{0j} are the oscillator strengths from the ground to the excited state while ϵ_{0i} and ϵ_{0j} are the excitation energies of the transitions. In general, the sum rule is a generalized sum which includes a sum over excitations to bound states and an integration taking into account excitations to continuum states. In the present work the sum rule is explicitly discretized. The accuracy of Eq. (3) depends on the reliability of the discretization of the f -value distribution.

For hydrogen, the f -value distribution is determined from a 30 states pseudostate expansion of the np excited state spectrum. This expansion predicts the dipole polarizability of H to be $4.50a_0^3$ with another eight trailing zeros. An expansion of identical size and accuracy for the f -value distribution for Ps was obtained by the simple expedient of rescaling the individual terms in the expansion by the appropriate values of 2. It is known that C_6 parameters derived from pseudostate calculations generally converge very quickly as the dimension of the pseudostate basis is increased [6,7].

For helium the f -value distribution was determined by using a large basis configuration interaction (CI) calculation for the ground state (1630 configurations) and then using another large CI calculation (2550 configurations) to determine the $^1P^o$ excited-state spectrum. This calculation gave a value for the He polarizability, $1.3833a_0^3$ that is about 0.1% larger than the converged *ab initio* value of $1.3819a_0^3$ [8]. The C_6 parameters resulting from the CI f -value distribution should be similarly accurate.

For the other rare gases recourse was made to a set of published pseudo-excitation-energies and dipole oscillator strengths [9]. The pairs of (f_{0i}, E_{0i}) were constrained to give f -value sum rules in agreement with empirical estimates of these sum rules [10]. For all practical purposes, these sets of empirical (f_{0i}, E_{0i}) are expected to give estimates of dispersion coefficients that are accurate to about 1% [9,10].

Besides the rare gases, C_6 has also been computed for some Ps-alkali-metal atom combinations. For these systems, it is necessary to take into consideration contributions from both the core and valence electrons. The contribution from the core was made using an approximation designed to give

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TABLE I. Atomic polarizabilities α_d (given in a_0^3) for atomic hydrogen, the rare gases, and the singly charged cores of the alkali-metal atoms. The Δ parameters (in hartrees) needed for the Koopmans model to reproduce the known polarizabilities are also listed.

System	α_d	Δ
H	4.5	-0.0286
He	1.383 [20]	0.2846
Ne	2.669 [20]	0.736
Ar	11.08 [20]	0.1814
Kr	16.79 [20]	0.112
Xe	27.16 [20]	0.0470
Li ⁺	0.1925 [21]	0.745
Na ⁺	0.99 [22]	1.12
K ⁺	5.47 [12,23]	0.156
Rb ⁺	9.076 [24]	0.0689

a reasonable estimate of the f -value distribution with a minimum of computation. We use the sum rule for the core polarizability, viz.,

$$\alpha_d = \sum_i \frac{f_{0i}}{\epsilon_{0i}^2} \quad (4)$$

to quickly estimate an f -value distribution function of reasonable accuracy. First we assume that the contribution from each closed subshell (N_i) is equal to the number of electrons in the subshell. Next, we assume the excitation energy for each shell to be equal to the Koopmans energy ϵ_i (i.e., the single particle energy coming from a Hartree-Fock calculation) plus an energy shift. Then, the identity

$$\alpha_d = \sum_i \frac{N_i}{(\epsilon_i + \Delta)^2} \quad (5)$$

is used to fix Δ so that the computed polarizability is equal to the experimentally known core polarizability. A tabulation of the values assigned to Δ and the underlying polarizabilities used to fix Δ is given in Table I. Estimates of Δ are also given for the rare gases.

For the valence electron, a model potential calculation was used to determine the wave function of the ground state and the $^2P^o$ excited states. The model potential adds a semiempirical polarization potential to the direct and exchange interactions of the Hartree-Fock core. The orbital basis set used to diagonalize the Hamiltonian was sufficiently large to give an exact description of the ground state and lowest $^2P^o$ excited states. The rest of the f -value distribution for the higher discrete and continuum states is given by the energies and oscillator strengths of what is essentially a pseudostate spectrum. The details of the semiempirical Hamiltonian have been described in numerous other calculations [11–14] and do not need to be recapitulated here. The static dipole polarizabilities given by the present calculations for Li, Na, K, and Rb are $164.2a_0^3$, $162.8a_0^3$, 290.0 , and $315.7a_0^3$, respectively. These are in good agreement with high-quality relativistic many-body perturbation theory (MBPT) calculations

TABLE II. The van der Waals coefficients for various Ps-X (and H-X) systems (in atomic units). Generally, the effective oscillator strength distribution (or the frequency dependent polarizability) for the first atom of every pair in the table is close to exact. The different columns refer to the method used to determine the oscillator strength distribution of the second atom for each pair.

System	Koopmans	Pseudostate or empirical	Other
Ps-H	36.021	34.785	34.785 ^a
Ps-He	13.83	13.37	13.34 ^a
Ps-Ne	27.93	26.74	
Ps-Ar	102.8	98.50	
Ps-Kr	150.7	144.1	
Ps-Xe	229.6	221.6	
Ps-Li		463.9	
Ps-Na		507.2	
Ps-K		768.3	
Ps-Rb		844.8	
H-H	6.816	6.4990	6.4990 ^b
H-He	2.977	2.8216	2.8213 ^b
H-Ne	6.218	5.64	5.688 ^c
H-Ar	21.13	19.82	19.86 ^c
H-Kr	30.41	28.48	29.15 ^c
H-Xe	44.98	42.67	44.14 ^c
H-Li		66.54	66.536 ^b
H-Na		74.18	73.83 ^d
H-K		112.0	111.2 ^d
H-Rb		124.6	124.3 ^d

^aPseudostate calculations from Ref. [2].

^bClose to exact estimates from Ref. [8].

^cMany-body perturbation theory [16].

^dRelativistic many-body perturbation theory [17].

giving $164.11a_0^3$ for Li [8], $163.1a_0^3$ for Na [15], $290.1a_0^3$ for K [15], and $317.4a_0^3$ for Rb [15].

The expression for the C_6 parameter for alkali-metal–Ps systems is

$$C_6 = \frac{3}{2} \sum_{ij} \frac{N_i f_{0j}}{(\epsilon_{0i} + \Delta) \epsilon_{0j} (\epsilon_{0j} + \Delta + \epsilon_{0i})} + \frac{3}{2} \sum_{ij} \frac{f_{0i} f_{0j}}{\epsilon_{0i} \epsilon_{0j} (\epsilon_{0j} + \epsilon_{0i})}. \quad (6)$$

More than 90% of the contributions to the C_6 parameter involve the valence excitations of the alkali-metal atom. Therefore, the uncertainty associated with the Koopmans approximation for the core in Eq. (6) is expected to be small.

The results of the present calculations for C_6 are listed in Table II. The present results for the Ps-H and Ps-He systems are in agreement at the 0.1% level with the previous calculations [2]. The C_6 parameters have also been computed for the H-H and H-He combinations and they are within 0.1% of the close to exact values of Yan *et al.* [8].

The values of C_6 for the Ps–rare-gas combinations listed in Table II have an accuracy comparable to the best estimates

of the dispersion coefficients for the H–rare-gas combinations. The present estimates of C_6 for the H–rare-gas combinations are probably the most accurate that have been published. Although, the most accurate *ab initio* calculations of C_6 are the MBPT calculations of Thakkar *et al.*, [16], the MBPT model overestimates the dipole polarizabilities of the heavier noble gases, Kr and Xe by a couple of percent. The empirical (f_{0i}, E_{0i}) set [9] for the noble gases used here reproduces the known dipole polarizabilities exactly.

It is instructive to compare the semiempirical estimates of the dispersion coefficient with those computed with the Koopmans approximation. For the rare gases, the Koopmans C_6 is generally a couple of percent larger than the semiempirical value. The Koopmans approximation provides a very quick way to generate a reasonable estimate for C_6 from the experimental dipole polarizability and Hartree-Fock single particle energies.

Given the high degree of accuracy of the f -value distributions for Ps and the alkali-metal atoms, one can expect that the dispersion coefficients reported in Table II have an accuracy of about 2% or better. Terms involving core excitations contribute less than 10% to C_6 , and since the Koopmans approximation is accurate to better than 5% to the rare gases, one can assert that use of the Koopmans approximation for the core results in an error that is probably less than 1%. This estimate of the accuracy is certainly consistent with the better than 1% agreement with the H–alkali-metal dispersion parameters that were computed using relativistic MBPT

[17]. The MBPT f -value distribution (in practice, the MBPT calculation used the frequency dependent dipole polarizability to compute C_6) is believed to produce polarizabilities and dispersion parameters that are accurate to better than 1% [15].

III. CONCLUSIONS

Estimates of the van der Waals coefficient C_6 have been made for various Ps-atom systems. Results for H and He are effectively exact and reproduce earlier calculations. The C_6 parameters for the rare gases and alkali-metal atoms should also be reliable with an expected uncertainty of 1–2%.

The present dispersion parameters have implications for the determination of the momentum transfer cross section for Ps–rare-gas scattering. At the present time, the only calculations [18,19] are performed in the fixed target approximation which results in a repulsive Ps-atom potential. However, the van der Waals interaction is attractive and Eq. (2) suggests a phase shift of about 0.12 rad at $k=0.5a_0^{-1}$. The van der Waals interaction should be taken into consideration before any definitive statements about the energy dependence of the momentum transfer cross section are made [18].

ACKNOWLEDGMENTS

The authors would like to thank J. C. Nou and C. Hoffman of NTU for workstation support.

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