van der Waals coefficients for positronium interactions with atoms

A. R. Swann,[*] J. A. Ludlow,[†] and G. F. Gribakin[‡]

Centre for Theoretical Atomic, Molecular, and Optical Physics, School of Mathematics and Physics,
Queen's University Belfast, Belfast BT7 1NN, United Kingdom

The random-phase approximation with exchange (RPAE) is used with a *B*-spline basis to compute dynamic dipole polarizabilities of noble-gas atoms and several other closed-shell atoms (Be, Mg, Ca, Zn, Sr, Cd, and Ba). From these, values of the van der Waals C_6 constants for positronium interactions with these atoms are determined and compared with existing data. After correcting the RPAE polarizabilities to fit the most accurate static polarizability data, our best predictions of C_6 for Ps–noble-gas pairs are expected to be accurate to within 1%, and to within a few percent for the alkaline-earth metals. We also used accurate dynamic dipole polarizabilities from the literature to compute the C_6 coefficients for the alkali-metal atoms. Implications of increased C_6 values for Ps scattering from more polarizable atoms are discussed.

I. INTRODUCTION

The interaction of positronium (Ps) with matter and antimatter is an important topic [1] with applications in many areas of physics. For instance, the proposed AEgIS experiment would produce an antihydrogen beam from the reaction between Ps and antiprotons [2,3]. The antihydrogen would then be used to determine whether antimatter is affected by gravity in the same manner as matter. Ps is widely used in condensed-matter physics to determine pore sizes in microporous materials and probe intermolecular voids in polymers [4]. Further, positronium formation in porous materials is used to study its interactions with gases, e.g., xenon [5,6], or the interaction between the Ps atoms themselves, with prospects of Bose-Einstein condensation at room temperature [7,8].

Here we focus on the problem of Ps-atom scattering. Compared with electron-atom scattering and positron-atom scattering, Ps-atom scattering is more difficult to treat theoretically, chiefly because both scattering objects have an internal structure [9].

In this paper we address low-energy Ps scattering from closed-shell atoms. The short-range Ps-atom interaction is repulsive, because (a) the Pauli principle prevents the electron from Ps from entering the volume occupied by the atomic electrons, and (b) the positron is repelled by the screened potential of the atomic nucleus. However, low-energy Ps-atom scattering is also affected by the attractive long-range van der Waals interaction [10–12].

The van der Waals potential behaves asymptotically as

$$U(R) \simeq -\frac{C_6}{R^6}, \tag{1}$$

where R is the distance between the centers of mass of the atoms, and C_6 is the van der Waals coefficient for the atomic pair [13]. The value of the C_6 constant determines

the scattering phase shifts for the partial waves $l \geqslant 2$ at low collision momenta k [14],

$$\delta_l(k) \simeq \frac{6 C_6 \pi k^4}{(2l-3)(2l-1)(2l+1)(2l+3)(2l+5)}. \tag{2}$$

The magnitude of C_6 also affects the Ps-atom scattering length A. This can be seen from the estimate which uses the potential (1) with a cutoff at $R = R_0$ [12],

$$A = \left(\frac{mC_6}{8}\right)^{1/4} \frac{\Gamma(3/4)}{\Gamma(5/4)} \frac{J_{-1/4}(x_0)}{J_{1/4}(x_0)}, \tag{3}$$

where m is the reduced mass, Γ and J_ν are the gamma and Bessel functions, respectively, and

$$x_0 = \frac{\sqrt{mC_6/2}}{R_0^2}. \tag{4}$$

The dimensional prefactor in Eq. (3) determines the characteristic magnitude of the scattering length in atomic collisions [15]. We use atomic units throughout, so that $m = 2$ for Ps-atom collisions.

Mitroy and Bromley [16] calculated the C_6 constants for Ps–noble-gas interactions using the oscillator strength sum rule. For He they calculated the oscillator strengths via the configuration interaction (CI) method, while for Ne, Ar, Kr, and Xe recourse was made to a set of published pseudo-excitation energies and dipole oscillator strengths [17], leading to semiempirical (SE) values of C_6. In a recent paper devoted to Ps scattering from Ar and Kr [12], Fabrikant and Gribakin used the London formula [18] for the van der Waals coefficients, which gave values about 6% greater than those from Ref. [16]. To estimate the effect of this difference on Ps-atom scattering we can use Eq. (3), which shows that for Ar ($R_0 = 2.67$ a.u. [12]), changing C_6 from 152 [12] to 144.1 a.u. [16] increases the scattering length by about 4%. This example shows that Ps-atom scattering is sensitive to the value of the van der Waals coefficient.

In this work, we employ the random-phase approximation with exchange (RPAE) [19,20] to calculate the dynamic dipole polarizabilities of the noble-gas atoms and several other closed-shell atoms with an ns^2 valence shell. These are used to calculate the C_6 constants for Ps-atom pairs

---

[*]aswann02@qub.ac.uk

[†]Present address: AquaQ Analytics, Suite 5, Sturgeon Building, 9–15 Queen Street, Belfast BT7 1NN, United Kingdom.

[‡]g.gribakin@qub.ac.uk

ab initio. The RPAE method, often called simply the random-phase approximation (RPA), is equivalent to the (linearized) time-dependent coupled Hartree-Fock method (see, e.g., Ref. [21] and references therein). RPAE is known to provide a good description of atomic polarization for the noble gases [22,23]. To make our predictions more accurate, we use scaling based on the known values of the static dipole polarizabilities. As a result, we expect our final C_6 constants to be accurate to better than 1%. As far as we are aware, there are currently no published values of C_6 for Ps interactions with other closed-shell atoms. Although the RPAE method is less accurate for them, our final C_6 values provide a good benchmark for future work.

II. THEORY

The van der Waals coefficient for a pair of atoms, A and B, may be expressed as

$$C_6 = \frac{2}{3} \sum_{n,n'} \frac{|\langle n_A|\mathbf{D}|0_A\rangle|^2 |\langle n'_B|\mathbf{D}|0_B\rangle|^2}{E_n^A + E_{n'}^B - E_0^A - E_0^B} \tag{5}$$

where $\mathbf{D}$ is the electric dipole operator, the matrix elements are taken between the ground (0) and excited (n or n') states of the atoms, with respective energies E_0 and E_n, and the extra indices (A or B) are used to distinguish the two atoms [24].

There exists a useful relationship connecting dynamic polarizabilities of imaginary frequencies with C_6. The dynamic polarizability at frequency ω is given by

$$\alpha(\omega) = \frac{1}{3} \sum_n \left(\frac{|\langle n|\mathbf{D}|0\rangle|^2}{E_n - E_0 - \omega - i\delta} + \frac{|\langle n|\mathbf{D}|0\rangle|^2}{E_n - E_0 + \omega + i\delta} \right), \tag{6}$$

where δ is a positive infinitesimal, which determines the sign of the imaginary part of $\alpha(\omega)$ for real frequencies ω above the ionization potential of the atom. The ground-state static polarizability is $\alpha(0)$. The van der Waals constant can be obtained by integrating the product of dynamic polarizabilities of atoms A and B over imaginary frequencies, viz.,

$$C_6 = \frac{3}{\pi} \int_0^\infty \alpha_A(i\omega)\alpha_B(i\omega)\,d\omega. \tag{7}$$

This result is very convenient because the integration path avoids the poles of the dynamic polarizabilities.

For hydrogenic atoms (such as H and Ps), the polarizabilities are given by Eq. (6) with the dipole matrix elements replaced by the single-particle radial matrix elements $\langle np|r|1s\rangle$, where r is either the electron-proton (H) or electron-positron (Ps) separation. Thus, for an interacting pair of hydrogenic atoms, an essentially exact value of C_6 can be found. However, for many-electron atoms (such as the noble gases) the single-particle (e.g., Hartree-Fock) method does not give accurate results. RPAE is a many-body theory method that is known to give accurate dipole polarizabilities and photoionization cross sections for closed-shell atoms, with the best results for the noble gases [19,22].

After the RPAE equations have been solved (see the appendix for details), the dynamic dipole polarizability is

calculated as

$$\alpha(\omega) = -\frac{2}{3} \left(\sum_{\nu > F, \mu \leqslant F} \frac{\langle \mu\|d\|\nu\rangle\langle\nu\|A(\omega)\|\mu\rangle}{\omega - \epsilon_\nu + \epsilon_\mu} \right.$$
$$\left. + \sum_{\nu \leqslant F, \mu > F} \frac{\langle \mu\|d\|\nu\rangle\langle\nu\|A(\omega)\|\mu\rangle}{-\omega + \epsilon_\nu - \epsilon_\mu} \right), \tag{8}$$

where $\langle\nu\|d\|\mu\rangle$ is the reduced Hartree-Fock dipole matrix element, $\langle\nu\|A(\omega)\|\mu\rangle$ is the reduced RPAE dipole matrix element, ϵ_ν is the energy of state ν, and $i\delta$ has been dropped for $\omega = 0$ and imaginary frequencies. In Eq. (8) the sums over the magnetic quantum numbers and spins have already been carried out, and the remaining sums are over the occupied ($\leqslant F$) or empty ($> F$) electron orbitals ν and μ.

Note that the matrix element $\langle\nu\|A(\omega)\|\mu\rangle$ is calculated off-mass-shell, i.e., for $\omega \neq \epsilon_\nu - \epsilon_\mu$, and the energy differences in the denominator of Eq. (8) contain the unperturbed Hartree-Fock energies. An equivalent but more complicated approach would be to calculate these amplitudes on the mass shell, simultaneously with finding the RPAE excitation energies $\omega_{\nu\mu}$. In this case the expression for the polarizability would contain modulus squared values of $\langle\nu\|A(\omega_{\nu\mu})\|\mu\rangle$ and the RPAE excitation energies in the denominator [cf. Eq. (6)].

The expressions for C_6 and $\alpha(\omega)$ contain sums over the complete sets of excited states. In real systems, such as atoms, these sets of excited states include both discrete, Rydberg states and the continuum of states with energies above the ionization potential of the system. By using B splines in a box of finite radius R (see Sec. III), the continuum is discretized in a way that allows accurate numerical calculations of the static polarizability (for $\omega = 0$), $\alpha(i\omega)$, and C_6.

III. NUMERICAL RESULTS

We use B splines to construct either hydrogenic or Hartree-Fock basis states. They provide an accurate representation of the ground-state orbitals and an effective spanning of the continuum, due to an appropriately chosen radial grid (see, e.g., Ref. [25]). In this work we use a set of 60 B splines of order 9, with a box size of $R = 15$ a.u. The absence of true continuum states does not affect the accuracy of $\alpha(0)$ or $\alpha(i\omega)$ because all excitations in the sums are virtual (the denominator never vanishes); such virtually excited electrons cannot travel away from the atom, so describing them by a set of states in a box is accurate.

We calculated static dipole polarizabilities of H, Ps, the noble gases, and other closed-shell atoms and compared them with exact theoretical or best experimental or theoretical values to verify the validity of the method. Then we computed dynamic polarizabilities $\alpha(i\omega_j)$ over a discrete set of imaginary frequencies

$$\omega_j = \omega_0[e^{\sigma(j-1)} - 1], \qquad j = 1, \ldots, N_\omega, \tag{9}$$

where ω_0, N_ω, and $\omega_{\max} \equiv \omega_{N_\omega}$ are parameters, and

$$\sigma = \frac{1}{N_\omega - 1} \ln\left(\frac{\omega_{\max}}{\omega_0} + 1 \right). \tag{10}$$

TABLE I. Static dipole polarizabilities $\alpha(0)$ for the noble gases and other closed-shell atoms (in atomic units).

Atom	Present	RPAE[a]	RRPA[b]	Rec.[c]	F[d]
He	1.322	1.256	1.322	1.384	1.047
Ne	2.377	2.30	2.38	2.67	1.123
Ar	10.758	10.73	10.77	11.07	1.029
Kr	16.476	16.18	16.47	17.075	1.036
Xe	27.099	27.98	26.97	27.815	1.026
Be	45.604	43.2	45.6	37.76	0.828
Mg	81.502		81.2	71.3	0.875
Ca	183.965	166	182.8	157.1	0.854
Zn	54.046		50.8	38.8	0.718
Sr	242.240		232.6	197.2	0.814
Cd	75.958		63.7	49.65	0.654
Ba	355.735		324.0	273.5	0.769

[a]This implementation [22,26] suffers from poor convergence.
[b]Relativistic random-phase approximation [27].
[c]Recommended experimental values for the noble gases, Zn, and Cd [28], and calculated values for alkaline-earth-metal atoms [29].
[d]F is the ratio of the recommended value to the present value.

Values of $\omega_0 = 0.01$ a.u., $N_\omega = 100$, and $\omega_{\max} = 1000$ a.u. have been used throughout; these values were chosen to provide accurate, converged values of the integral (7). For H and Ps the polarizabilities were calculated essentially exactly; for the noble gases and ns^2 atoms they were calculated using the RPAE method. The values of C_6 were then found by evaluating Eq. (7) numerically.

The static polarizability obtained for H was $\alpha(0) = 4.500$ a.u., in perfect agreement with the exact value of $\alpha(0) = 9/2$ [24]. The B-spline states and dipole amplitudes for hydrogen can be used to calculate $\alpha(0)$ and $\alpha(i\omega)$ for Ps by halving the energies and doubling the amplitudes (due to the reduced mass of Ps being a half of that of H). This gives $\alpha(0) = 36$ a.u. for Ps.

Table I shows the static polarizabilities obtained using RPAE for the noble-gas and other closed-shell atoms. The RPAE static polarizabilities for the noble-gas atoms agree to 0.1% or better with the results of the equivalent coupled Hartree-Fock calculation [30], with the present values for Kr and Xe being more accurate numerically due to better convergence. The results are also in agreement with calculations made using the relativistic random-phase approximation (RRPA, which also accounts for exchange). Larger differences are to be expected for heavier atoms, since relativistic corrections scale as $(Z/137)^2$, where Z is the nuclear charge. However, even for the heaviest noble-gas atom (Xe) the difference is less than 0.5%. This bodes well for using the dynamic polarizabilities to calculate the C_6 coefficients for Ps–noble-gas pairs. As expected, for the ns^2 atoms, the agreement with RRPA is poorer for heavier atoms (since the s electrons are affected more strongly by the relativistic corrections). The agreement with the experimental values for these atoms is also poorer in general. This is related to the smaller ionization potentials and larger effect of the non-RPA correlation effects (e.g., two-hole–two-particle excitations) in these systems.

The results for C_6 are displayed in Table II. Our calculations which use RPAE polarizabilities ("Present" in Table II)

TABLE II. van der Waals C_6 coefficients for various Ps-X systems (in atomic units).

System	Present	Best prediction[a]	CI/SE[b]	Other[c]
Ps-H	34.785		34.785	34.785
Ps-Ps	207.969			207.966
Ps-He	12.849	13.41	13.37	14.6
Ps-Ne	23.759	26.48	26.74	27.4
Ps-Ar	96.212	98.69	98.50	104.4
Ps-Kr	142.185	146.71	144.1	155.1
Ps-Xe	222.355	227.38	221.6	240.6
Ps-Be	241.416	208.6	210.7	294.3
Ps-Mg	393.484	355.8	357.9	506.4
Ps-Ca	717.138	641.5	636.6	1079
Ps-Zn	300.756	231.4		303.8
Ps-Sr	885.425	767.5	763.8	1144
Ps-Cd	397.161	285.0		381.6
Ps-Ba	1164.429	975.6	966.8	1569

[a]Obtained by scaling the matrix elements by ξ and energies by $1/\xi^2$, where $\xi = F^{1/4}$ (see Table I).
[b]Computed in Ref. [16] using the configuration interaction (CI) for He and semiempirical dipole polarizabilities [17] for the noble gases, and in the present work, using empirically adjusted CI + many-body theory data [31] for the alkaline-earth-metal atoms.
[c]For Ps-H and Ps-Ps: pseudostate calculations [32]. For all other systems, these values were calculated using the London formula $C_6 = 3\alpha_A\alpha_B I_A I_B/[2(I_A + I_B)]$, where $\alpha_{A,B}$ and $I_{A,B}$ are the static dipole polarizabilities and ionization potentials of the atoms [18]; the polarizabilities were taken from Ref. [28] and the ionization potentials were taken from Ref. [33].

are in close agreement with the SE calculations of Mitroy and Bromley [16] for the heavier noble gases; the relative differences for Ps-Ar, Ps-Kr, and Ps-Xe are 2%, 1%, and 0.3% respectively. For the lighter noble gases the differences are more significant: 4% and 11% for Ps-He and Ps-Ne, respectively. This discrepancy can be traced back to the fact that the RPAE polarizabilities for He and Ne are lower than the recommended values, by 5% and 12%, respectively. Correcting the RPAE C_6 value for He by the corresponding factor F (see Table I) gives $C_6 = 13.45$, which agrees with the accurate value for He from Ref. [16] to within 0.6%. However, this crude scaling violates the Thomas-Reiche-Kuhn sum rule, which in the limit of large ω gives

$$\alpha(i\omega) \simeq \frac{N}{\omega^2}, \tag{11}$$

where N is the number of atomic electrons. A better approach is to scale the dipole matrix elements $\langle\mu\|d\|\nu\rangle$ and $\langle\nu\|A(\omega)\|\mu\rangle$ in Eq. (8) by some factor ξ and the orbital energies in the denominators by $1/\xi^2$. In this case the sum rule is preserved, while the calculated static polarizability is scaled by ξ^4. The appropriate choice of ξ is given by $\xi = F^{1/4}$. Carrying out this scaling for He gives $C_6 = 13.41$, which agrees with the value from Ref. [16] to within 0.3%. This is a clear improvement over the simple scaling by a factor of F.

As a further test of the effectiveness of this scaling, the C_6 constants were calculated for pairs of the noble-gas and alkaline-earth-metal atoms. These were compared with data

TABLE III. van der Waals C_6 coefficients for Ps-alkali-metal systems (in atomic units).

Atom	Li	Na	K	Rb	Cs	Fr
$C_6{}^a$	462.8	505.7	765.7	846.8	1014.6	937.5
$C_6{}^b$	463.9	507.2	768.3	844.8		

[a]Computed in the present work using empirically adjusted many-body theory data [31].
[b]Semiempirical calculations from Ref. [16].

from Ref. [31], wherein several relativistic many-body theory [29,34] and semiempirical [17] methods were employed. For noble-gas pairs, the minimum relative difference was 0.7% (for Ar-Ar), while the maximum (for Xe-Xe) was 5% (due to the use of the dynamical polarizability "normalized" to $\alpha(0) = 27.16$ a.u. [17] in Ref. [31], which is lower than the recommended experimental value $\alpha(0) = 27.815$ a.u. that we use). For alkaline-earth-metal pairs, the comparison was actually better; the relative differences ranged from 0.2% (for Sr-Sr) to 2.1% (for Be-Be). This is because we use the same recommended static polarizabilities for the alkaline-earth-metal atoms as in Ref. [31].

Scaling the *ab initio* RPAE polarizabilities in this way produces our best prediction of the C_6 van der Waals coefficients (third column in Table II). We expect that for the noble-gas atoms these values are accurate to within 1%. The relative differences from the CI/SE values of Mitroy and Bromley for Ne, Ar, Kr, and Xe are 1%, 0.2%, 1.8%, and 2.6%, respectively. We believe that for Kr and Xe our best prediction values are superior to those of Ref. [16], where the polarizabilities from Ref. [17] were used.

Since the RPAE polarizabilities of the ns^2 atoms are greater than the recommended values of $\alpha(0)$ by 15–50%, the calculated *ab initio* C_6 values significantly overestimate the true van der Waals coefficients. Given the larger discrepancy for $\alpha(0)$, the use of scaling is a cruder procedure for improving the C_6 constants. In this case we believe that our best predictions are accurate within few percent for the alkaline-earth-metal atoms, and within 5–10% for Zn and Cd.

As a further test of the accuracy of our predictions for the alkaline-earth-metal atoms, we used tabulated dynamic dipole polarizabilities from Ref. [31], which were computed using a combination of relativistic methods, including RRPA, CI, and many-body perturbation theory, and further adjusted using accurate theoretical and experimental data. These values are presented in the fourth column of Table II (lower half). In all cases the difference between these values and our best predictions does not exceed 1%. Reference [31] also presents accurate dynamic dipole polarizabilities for the alkali-metal atoms, and we used these to compute the C_6 coefficients for the Ps-alkali-metal pairs; see Table III. Comparison with semiempirical calculations presented in Ref. [16] shows excellent agreement.

Looking at the last column in Table II, we see that the London formula does a reasonable job for the more rigid noble-gas atoms but tends to overestimate the C_6 coefficients significantly for Ps interacting with ns^2 atoms.

IV. CONCLUSIONS

Dynamic dipole polarizabilities over a range of imaginary frequencies were computed numerically exactly for H and Ps, and by using RPAE for the noble-gas atoms and several other closed-shell atoms. The static polarizabilities for the noble gases deviated from relativistic (RRPA) calculations by no more than 0.5%, and for Ar, Kr, and Xe were within few percent of experimental values. There was greater error for the other closed-shell atoms, but this was expected; the RPAE method is most suitable for the noble gases.

Ab initio calculations of the van der Waals C_6 coefficients for Ps interactions with these atoms were performed. For the heavier noble gases, close agreement is observed with previous calculations [16]. For the lighter noble gases (He and Ne) the discrepancies are more significant, which motivates a sum rule preserving scaling of the dynamical polarizabilities to calculate C_6 values. Though these data are no longer *ab initio*, they are expected to the be the most accurate values currently available. For the most part, our values of C_6 for Ps interactions with the ns^2 atoms differ significantly from the London values. Here our best prediciton are less accurate (few to 10%), but as there are no other theoretical calculations of these data, these values will provide a useful benchmark for future calculations.

It is interesting to discuss the implications of the C_6 values for low-energy Ps-atom scattering. It is clear from Table II that for more polarizable (and more weakly bound) atoms, the C_6 values are greater, and that Ps will experience a stronger van der Waals attraction to these atoms. However, it can be seen from the parameter x_0, Eq. (4), which determines the scattering length in Eq. (3), that the increase in C_6 for such atoms is offset by the increase in the parameter R_0, which is proportional to the atomic radius. In fact, the latter effect makes x_0 smaller for the more weakly bound atoms. As a result, the more polarizable atoms are not more attractive for Ps, and will likely have larger positive Ps scattering lengths, due to their larger geometric sizes. This also shows that Ps binding to closed-shell neutral atoms does not occur. Note that this is in contrast to many open-shell atoms, e.g., Na, Cu, or the halogens, which do bind Ps by accommodating the extra electron in their valence shell [35,36]. However, even in the case of Ps bound states with alkali-metal atoms, the binding energy decreases in the sequence PsLi, PsNa, PsK [37], in spite of the greater values of the C_6 constant. This is primarily the effect of the increasing atomic radius.

It is hoped that the results presented here will be useful for studies of Ps-noble-gas-atom scattering and Ps interactions with ns^2 and alkali-metal atoms. With little extra work, the method can be extended to calculate quadrupole and higher polarizabilities and determine higher-order van der Waals coefficients C_8 and C_{10}.

APPENDIX: RPAE EQUATIONS

In the equations for the RPAE dipole matrix element $\langle \nu | A(\omega) | \mu \rangle$, we must distinguish between the hole states, i.e.,

states below the Fermi level F, and particle states, i.e., states above the Fermi level F. For $\nu > F$ and $\mu \leqslant F$ we have

$$\langle \nu | A(\omega) | \mu \rangle = \langle \nu | d | \mu \rangle + \left(\sum_{\nu' > F, \mu' \leqslant F} - \sum_{\mu' > F, \nu' \leqslant F} \right) \frac{\langle \nu \mu' | V | \nu' \mu \rangle - \langle \mu' \nu | V | \nu' \mu \rangle}{\omega - \epsilon_{\nu'} + \epsilon_{\mu'} + i(1 - 2n_{\nu'})\delta} \langle \nu' | A(\omega) | \mu' \rangle, \tag{A1}$$

and a formally identical equation for $\nu \leqslant F$ and $\mu > F$.

In Eq. (A1), $\langle \nu | d | \mu \rangle$ is the Hartree-Fock dipole matrix element; $\langle \nu \mu' | V | \nu' \mu \rangle$ is the Coulomb matrix element, which is defined by

$$\langle \nu \mu' | V | \nu' \mu \rangle \equiv \iint \varphi_\nu^*(\mathbf{r}) \varphi_{\mu'}^*(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \varphi_{\nu'}(\mathbf{r}') \varphi_\mu(\mathbf{r}) \, d^3\mathbf{r} \, d^3\mathbf{r}', \tag{A2}$$

where the φ_ν are single-particle wave functions; $\epsilon_{\nu'}$ is the energy of state ν'; and

$$n_{\nu'} = \begin{cases} 0 & \text{for} \quad \nu' > F, \\ 1 & \text{for} \quad \nu' \leqslant F. \end{cases} \tag{A3}$$

By separating the angular and radial parts in the electronic states φ, and then integrating over the angular variables and summing over the magnetic quantum numbers and spins, one obtains the RPAE equations for the *reduced* amplitudes $\langle \nu \| A(\omega) \| \mu \rangle$ in the form

$$\langle \nu \| A(\omega) \| \mu \rangle = \langle \nu \| d \| \mu \rangle + \frac{1}{3} \left(\sum_{\nu' > F, \mu' \leqslant F} - \sum_{\mu' > F, \nu' \leqslant F} \right) \frac{\langle \nu \mu' \| U_1 \| \nu' \mu \rangle \langle \nu' \| A(\omega) \| \mu' \rangle}{\omega - \epsilon_{\nu'} + \epsilon_{\mu'} + i(1 - 2n_{\nu'})\delta}, \tag{A4}$$

where

$$\langle \nu \| d \| \mu \rangle = (-1)^{l_\nu} \sqrt{[l_\nu][l_\mu]} \begin{pmatrix} l_\nu & 1 & l_\mu \\ 0 & 0 & 0 \end{pmatrix} \int_0^R P_\nu(r) \, r \, P_\mu(r) \, dr, \tag{A5}$$

$$\langle \nu \mu' \| U_1 \| \nu' \mu \rangle = 2 \langle \nu \mu' \| V_1 \| \nu' \mu \rangle - 3 \sum_{l=0}^\infty (-1)^{l-1} \begin{Bmatrix} l_\nu & 1 & l_\mu \\ l_{\mu'} & l & l_{\nu'} \end{Bmatrix} \langle \nu \mu' \| V_l \| \mu \nu' \rangle, \tag{A6}$$

and

$$\langle \nu \mu' \| V_l \| \nu' \mu \rangle = \sqrt{[l_\nu][l_{\mu'}][l_{\nu'}][l_\mu]} \begin{pmatrix} l_\nu & l & l_\mu \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_{\mu'} & l & l_{\nu'} \\ 0 & 0 & 0 \end{pmatrix} \int_0^R \int_0^R P_\nu(r) P_{\mu'}(r') \frac{r_<^l}{r_>^{l+1}} P_{\nu'}(r') P_\mu(r) \, dr \, dr' \tag{A7}$$

are the reduced dipole and Coulomb matrix elements, $P_\nu(r)$ are radial wave functions, $[l_\nu] \equiv 2l_\nu + 1$, $r_> = \max(r, r')$, $r_< = \min(r, r')$, and R is the box radius in our B-spline-basis implementation.

Introducing vectors x and y for $\langle \nu \| A(\omega) \| \mu \rangle$ for $\nu > F$, $\mu \leqslant F$ and $\nu \leqslant F$, $\mu > F$, respectively, we can write Eq. (A4) in block matrix form as

$$\begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} d \\ d \end{pmatrix} + \begin{pmatrix} U_{1a} & U_{1b} \\ U_{1b} & U_{1a} \end{pmatrix} \begin{pmatrix} \chi_1 & 0 \\ 0 & \chi_2 \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}, \tag{A8}$$

where χ_1 and χ_2 are the diagonal matrices of energy denominators, d is the vector of Hartree-Fock dipole matrix elements, and the matrices U_{1a} and U_{1b} represent the two terms in Eq. (A6). This linear equation can be solved numerically for the RPAE dipole amplitudes, and then the dynamic dipole polarizability is calculated from Eq. (8).

[1] G. Laricchia and H. R. J. Walters, Riv. Nuovo Cimento **35**, 305 (2012).

[2] A. Kellerbauer, M. Amoretti, A. Belov, G. Bonomi, I. Boscolo, R. Brusa, M. Büchner, V. Byakov, L. Cabaret, C. Canali, C. Carraro, F. Castelli, S. Cialdi, M. de Combarieu, D. Comparat, G. Consolati, N. Djourelov, M. Doser, G. Drobychev, A. Dupasquier, G. Ferrari, P. Forget, L. Formaro, A. Gervasini, M. Giammarchi, S. Gninenko, G. Gribakin, S. Hogan, M. Jacquey, V. Lagomarsino, G. Manuzio, S. Mariazzi, V. Matveev, J. Meier, F. Merkt, P. Nedelec, M. Oberthaler, P. Pari, M. Prevedelli, F. Quasso, A. Rotondi, D. Sillou, S. Stepanov, H. Stroke, G. Testera, G. Tino, G. Trénec, A. Vairo, J. Vigué, H. Walters, U. Warring, S. Zavatarelli, and D. Zvezhinskij, Nucl. Instrum. Methods B **266**, 351 (2008).

[3] G. Consolati, R. Ferragut, A. Galarneau, F. Di Renzo, and F. Quasso, Chem. Soc. Rev. **42**, 3821 (2013).

[4] D. W. Gidley, H.-G. Peng, and R. S. Vallery, Ann. Rev. Mat. Res. **36**, 49 (2006).

[5] K. Shibuya, T. Nakayama, H. Saito, and T. Hyodo, Phys. Rev. A **88**, 012511 (2013).

[6] K. Shibuya, Y. Kawamura, and H. Saito, Phys. Rev. A **88**, 042517 (2013).

[7] A. P. Mills, Jr., Rad. Phys. Chem. **76**, 76 (2007).

[8] D. B. Cassidy and A. P. Mills, Jr., Phys. Rev. Lett. **100**, 013401 (2008).

[9] H. S. W. Massey and C. B. O. Mohr, Proc. Phys. Soc. Sec. A **67**, 695 (1954).

[10] J. Mitroy and I. A. Ivanov, Phys. Rev. A **65**, 012509 (2001).

[11] J. Mitroy and M. W. J. Bromley, Phys. Rev. A **67**, 034502 (2003).

[12] I. I. Fabrikant and G. F. Gribakin, Phys. Rev. A **90**, 052717 (2014).

[13] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics: Nonrelativistic Theory*, 2nd ed. (Pergamon Press, Oxford, 1965).

[14] P. S. Ganas, Phys. Rev. A **5**, 1684 (1972).

[15] G. F. Gribakin and V. V. Flambaum, Phys. Rev. A **48**, 546 (1993).

[16] J. Mitroy and M. W. J. Bromley, Phys. Rev. A **68**, 035201 (2003).

[17] A. Kumar and W. J. Meath, Mol. Phys. **54**, 823 (1985).

[18] F. London, Trans. Faraday Soc. **33**, 8B (1937).

[19] M. Ya. Amusia, N. A. Cherepkov, and L. V. Chernysheva, Zh. Eksp. Teor. Fiz. **60**, 160 (1971) [Sov. Phys. JETP **33**, 90 (1971)].

[20] M. Ya. Amusia, *Atomic Photoeffect* (Plenum, New York, 1990).

[21] F. Visser, P. E. S. Wormer, and P. Stam, J. Chem. Phys. **79**, 4973 (1983).

[22] M. Ya. Amusia, N. A. Cherepkov, and S. Shapiro, Zh. Eksp. Teor. Fiz. **63**, 889 (1972) [Sov. Phys. JETP **36**, 468 (1973)].

[23] J. Ludlow, Ph.D. thesis, Queen's University Belfast, 2003 (unpublished).

[24] V. B. Berestetskii, E. M. Lifshitz, and L. P. Pitaevskii, *Quantum Electrodynamics*, 2nd ed. (Pergamon Press, Oxford, 1982).

[25] G. F. Gribakin and J. Ludlow, Phys. Rev. A **70**, 032720 (2004).

[26] M. Ya. Amusia and N. A. Cherepkov, Case Studies At. Phys. **5**, 47 (1975).

[27] D. Kolb, W. R. Johnson, and P. Shorer, Phys. Rev. A **26**, 19 (1982).

[28] P. Schwerdtfeger, in *Computational Aspects of Electric Polarizability Calculations: Atoms, Molecules, and Clusters*, edited by G. Maroulis (IOS Press, Amsterdam, 2006), pp. 1–32; updated static dipole polarizabilities are available as a PDF file from the CTCP website at Massey University, http://ctcp.massey.ac.nz/dipole-polarizabilities.

[29] S. G. Porsev and A. Derevianko, Zh. Eksp. Teor. Fiz. **129**, 227 (2006) [Sov. Phys. JETP **102**, 195 (2006)].

[30] R. P. McEachran, A. D. Stauffer, and S. Greita, J. Phys. B **12**, 3119 (1979).

[31] A. Derevianko, S. G. Porsev, and J. F. Babb, At. Data Nucl. Data Tables **96**, 323 (2010).

[32] D. W. Martin and P. A. Fraser, J. Phys. B **13**, 3383 (1980).

[33] D. R. Lide (ed.), *CRC Handbook of Chemistry and Physics*, 89th ed. (CRC Press, Boca Raton, FL, 2008–2009).

[34] S. G. Porsev and A. Derevianko, Phys. Rev. A **65**, 020701 (2002).

[35] J. Mitroy, M. W. J. Bromley, and G. G. Ryzhikh, J. Phys. B **35**, R81 (2002).

[36] J. A. Ludlow and G. F. Gribakin, Int. Rev. At. Mol. Phys. **1**, 73 (2010).

[37] J. Mitroy and G. Ryzhikh, J. Phys. B **32**, 3839 (1999).