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## Revisiting the divergent multipole expansion of atom-surface interactions: Hydrogen and positronium, $\alpha$ -quartz, and physisorption

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We revisit the derivation of multipole contributions to the atom-wall interaction previously presented in Łach *et al.* [G. Łach, M. DeKieviet, and U. D. Jentschura, *Phys. Rev. A* **81**, 052507 (2010)]. A careful reconsideration of the angular momentum decomposition of the second-, third-, and fourth-rank tensors composed of the derivatives of the electric-field modes leads to a modification for the results for the quadrupole, octupole, and hexadecupole contributions to the atom-wall interaction. Asymptotic results are given for the asymptotic long-range forms of the multipole terms, in both the short-range and long-range limits. Calculations are carried out for hydrogen and positronium in contact with  $\alpha$ -quartz; a reanalysis of analytic models of the dielectric function of  $\alpha$ -quartz is performed. Analytic results are provided for the multipole polarizabilities of hydrogen and positronium. The quadrupole correction is shown to be numerically significant for atom-surface interactions. The expansion into multipoles is shown to constitute a divergent, asymptotic series. Connections to van der Waals corrected density-functional theory and applications to physisorption are described.

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### I. INTRODUCTION

Multipole corrections to the atom-surface interactions have been considered in Ref. [1], with an application to helium interacting with  $\alpha$ -quartz. The theory of atom-surface interactions is well known, for both perfect conductors as well as realistic dielectric materials (see Refs. [2–9], pp. 261–263 of Ref. [10], and Ref. [1]). In Ref. [1], the quadrupole, octupole, and hexadecupole contributions to the atom-wall interaction were evaluated. Here, we update the analysis presented in Ref. [1] with an emphasis on the isolation of angular momentum components of the quantized electric field near the wall.

Let us discuss the basis for the update, in terms of the initial expressions used for the evaluations, both for the cases discussed in Ref. [1] as well as for the modifications discussed here. Specifically, according to Eq. (22) of Ref. [1] (in accordance with Ref. [10]), the dipole part of the atom-wall interaction can be expressed as follows:

$$\mathcal{E}_{\ell=1} = -\frac{1}{2} \sum_{\vec{k}\lambda} \sum_i \alpha_{\ell=1}(\omega) |E_{\vec{k}\lambda}^i(\vec{r})|^2, \quad (1)$$

where  $\vec{E}_{\vec{k}\lambda}(\vec{r})$  is the (in general complex) mode function of the electric field near the wall,  $\vec{k}$  is the wave vector, and  $\lambda$  is the polarization. The index  $i$  enumerates the Cartesian components. The dipole polarizability of the atom is  $\alpha_{\ell=1}(\omega) = \alpha_1(\omega)$ , and it is evaluated at the angular frequency  $\omega = \omega_k = c|\vec{k}|$ , where  $c$  is the speed of light. The mode function  $\vec{E}_{\vec{k}\lambda}(z)$  of the electric field is related to the mode function  $\vec{A}_{\vec{k}\lambda}(z)$  of the vector potential by the relation

$$\vec{E}_{\vec{k}\lambda}(\vec{r}) = i\omega_k \vec{A}_{\vec{k}\lambda}(\vec{r}), \quad (2)$$

with the mode functions in Eqs. (18)–(20) of Ref. [1]. The formalism for the treatment of the dipole contribution is well established.

The starting point for the analysis of the quadrupole, octupole, and hexadecupole corrections to the atom-wall interaction has been given by Eq. (8) of Ref. [1] as follows:

$$\mathcal{E}_{\ell=2} = -\frac{1}{12} \sum_{\vec{k}\lambda} \sum_{ij} \alpha_2(\omega) |\nabla^j E_{\vec{k}\lambda}^i(\vec{r})|^2, \quad (3)$$

where  $\nabla^j \equiv \partial/\partial x^j$  and the indices  $i$  and  $j$  stand for the Cartesian components, and  $\alpha_2$  is the quadrupole polarizability of the atom. We reserve the index  $i$  for the component of the electric field. The octupole energy shift has been analyzed in Ref. [1] based on the expression

$$\mathcal{E}_{\ell=3} = -\frac{1}{180} \sum_{\vec{k}\lambda} \sum_{ijk} \alpha_3(\omega) |\nabla^j \nabla^k E_{\vec{k}\lambda}^i(\vec{r})|^2, \quad (4)$$

where  $\alpha_3 = \alpha_{\ell=3}$  is the octupole polarizability of the atom. The expressions (3) and (4) need to be substantiated by the specification of the angular momentum component relevant to the analysis. Namely, the virtual atomic transitions contributing to the quadrupole, octupole, and hexadecupole polarizabilities of the atom connect the atomic ground state to virtual states with angular momenta  $\ell = 2$  and 3. However, when one calculates sums such as

$$\sum_{ij} |\nabla^j E_{\vec{k}\lambda}^i(\vec{r})|^2, \quad (5)$$

without separating the ( $\ell = 2$ ) component of the second-rank tensor  $\nabla^j E^i$  first, then one sums over the  $\ell = 0$  and 1 components of the second-rank tensor  $T^{ji} = \nabla^j E^i$  as well. While the proper isolation of the angular momentum components does not change the functional form of the results reported in Ref. [1], some prefactors receive modifications. For the quadrupole term, the proper isolation of the  $\ell = 2$  component

leads to the modified expression

$$\mathcal{E}_{\ell=2} = -\frac{1}{12} \sum_{\bar{k}\lambda} \sum_{ij} \alpha_2(\omega) \left| \left\{ \nabla^j E_{\bar{k}\lambda}^i(\vec{r}) \right\} \Big|_{\ell=2} \right|^2 \quad (6)$$

where the  $\ell = 2$  component of a tensor is given by the traceless, symmetric component as follows:

$$T^{ij}|_{\ell=2} = \frac{1}{2} (T^{ij} + T^{ji}) - \frac{1}{3} \delta^{ij} \text{Tr}(T), \quad (7)$$

$\delta^{ij}$  is the Kronecker delta, and  $\text{Tr}(T) = \sum_i T^{ii}$  is the trace. The octupole term is substantiated by the expression

$$\mathcal{E}_3 = -\frac{1}{180} \sum_{\bar{k}\lambda} \sum_{ijk} \alpha_3(\omega) \left| \left\{ \nabla^j \nabla^k E_{\bar{k}\lambda}^i(\vec{r}) \right\} \Big|_{\ell=3} \right|^2, \quad (8)$$

where the isolation of the octupole ( $\ell = 3$ ) component of a third-rank tensor has recently been discussed by Itin and Reches in Ref. [11]. The isolation of the  $\ell = 3$  component of a third-rank tensor is not completely trivial. The modified expressions given in Eqs. (6) and (8) have phenomenological consequences which are discussed in the following.

Finally, the hexadecupole energy shift is calculated as follows:

$$\mathcal{E}_4 = -\frac{1}{5040} \sum_{\bar{k}\lambda} \sum_{ijk} \alpha_4(\omega) \left| \left\{ \nabla^j \nabla^k \nabla^l E_{\bar{k}\lambda}^i(\vec{r}) \right\} \Big|_{\ell=4} \right|^2. \quad (9)$$

The isolation of the  $\ell = 4$  component from a Cartesian tensor is discussed in Ref. [12].

We use Système International (SI mksA) units in the following, before we switch to atomic units in Sec. IV. The basis for the treatment of multipole interactions is discussed in Sec. II, the case of a perfect conductor is discussed in Sec. II B, and dielectric materials are discussed in Sec. III. Interactions with hydrogen and positronium atoms are discussed in Sec. IV. Conclusions are drawn in Sec. V.

## II. MULTIPOLE INTERACTIONS

### A. General formulation

In order to put things into perspective, and in terms of some orientation, we briefly review the concept of the multipole oscillator strength, inspired by Chap. 5 of Ref. [13]. The  $2^\ell$ -pole polarizability is written as

$$\alpha_\ell(\omega) = \frac{1}{2\ell+1} \sum_m \left\langle 1S \left| Q_{\ell m} \left( \frac{1}{H - E_{1S} + \hbar\omega} + \frac{1}{H - E_{1S} - \hbar\omega} \right) Q_{\ell m}^* \right| 1S \right\rangle, \quad (10)$$

where the  $Q_{\ell m}$  tensor is given as

$$Q_{\ell m} = \sum_a e \sqrt{\frac{4\pi}{2\ell+1}} r_a Y_{\ell m}(\hat{r}_a), \quad (11)$$

the  $r_a$  are the electron coordinates, and the sum over  $a$  runs over the atomic electrons. The spherical harmonic is  $Y_{\ell m}$ , and the shorthand notation  $\hat{r}_a$  summarizes the polar and azimuthal angles  $\theta_a$  and  $\varphi_a$  which define  $\hat{r}_a$  uniquely, and vice versa. Here,

$$T^{ij}|_{\ell=2} = \frac{1}{2} (T^{ij} + T^{ji}) - \frac{1}{3} \delta^{ij} \text{trc}(T) \quad (12)$$

is the traceless quadrupole component of a general tensor  $T^{ij}$ . The octupole energy shift ( $\ell = 3$ ) is evaluated according to Eq. (8):

$$\mathcal{E}_3 = -\frac{1}{180} \sum_{\bar{k}\lambda} \sum_{ijk} \alpha_3(\omega) \left| \left\{ \nabla^j \nabla^k E_{\bar{k}\lambda}^i(\vec{r}) \right\} \Big|_{\ell=3} \right|^2. \quad (13)$$

The  $\ell = 3$  component can be extracted from a third-rank tensor  $T^{ijk}$  as follows. One first decomposes  $T^{ijk}$  into a totally symmetric part  $S^{ijk}$ , a totally skew-symmetric part  $A^{ijk}$ , and a remainder term  $N^{ijk}$ :

$$S^{ijk} = T^{(ijk)} \quad (14a)$$

$$= \frac{1}{6} (T^{ijk} + T^{jki} + T^{kij} + T^{jik} + T^{kji} + T^{ikj}),$$

$$A^{ijk} = T^{[ijk]} \quad (14b)$$

$$= \frac{1}{6} (T^{ijk} + T^{jki} + T^{kij} - T^{jik} - T^{kji} - T^{ikj}),$$

$$N^{ijk} = T^{[ijk]} - S^{ijk} - A^{ijk}. \quad (14c)$$

The matrix  $S^{ijk}$  contains both components with  $\ell = 1$  and 3. One then forms a vector  $\alpha^k$  which one promotes to a matrix  $K^{ijk}$ :

$$\alpha^k = \delta^{ij} S^{ijk} = \frac{1}{3} (\delta^{ij} T^{ijk} + \delta^{ij} T^{ikj} + \delta^{ij} T^{kij}),$$

$$K^{ijk} = \frac{1}{5} (\alpha^i \delta^{jk} + \alpha^j \delta^{ik} + \alpha^k \delta^{ij}). \quad (15)$$

Finally, the  $\ell = 3$  component which we need for our considerations is obtained as

$$T^{ijk}|_{\ell=3} = S^{ijk} - K^{ijk}. \quad (16)$$

For the hexadecupole energy shift, we need the  $\ell = 4$  component of the Cartesian tensor:

$$T^{ijk\ell} = \nabla^i \nabla^j \nabla^k E_{\bar{k}\lambda}^\ell(\vec{r}). \quad (17)$$

It can be calculated as follows [12]:

$$\begin{aligned} T^{ijk\ell}|_{\ell=4} &= T^{(ijk\ell)} - \frac{1}{7} (\delta^{ij} T^{(\rho\rho k\ell)} + \delta^{ik} T^{(\rho\rho j\ell)} + \delta^{il} T^{(\rho\rho jk)} \\ &\quad + \delta^{jk} T^{(\rho\rho i\ell)} + \delta^{jl} T^{(\rho\rho ik)} + \delta^{k\ell} T^{(\rho\rho ij)}) \\ &\quad + \frac{1}{35} (\delta^{ij} \delta^{k\ell} + \delta^{ik} \delta^{j\ell} + \delta^{il} \delta^{jk}) T^{(\rho\rho\sigma\sigma)}. \end{aligned} \quad (18)$$

Here, the Einstein summation is understood, with dummy indices ( $\rho$  and  $\sigma$ ) being summed over. Furthermore, the symmetrization of a tensor is defined as follows:

$$\begin{aligned} T^{(ijk\ell)} &= \frac{1}{24} [T^{ijk\ell} + T^{ij\ell k} + T^{ikj\ell} + T^{ik\ell j} + T^{i\ell jk} + T^{i\ell k j} + T^{j i k \ell} + T^{j i \ell k} + T^{j k i \ell} + T^{j k \ell i} + T^{j \ell i k} + T^{j \ell k i} + T^{k i j \ell} + T^{k i \ell j} \\ &\quad + T^{k j i \ell} + T^{k j \ell i} + T^{k \ell i j} + T^{k \ell j i} + T^{\ell i j k} + T^{\ell i k j} + T^{\ell j i k} + T^{\ell j k i} + T^{\ell k j i} + T^{\ell k i j}]. \end{aligned} \quad (19)$$

For the case  $\ell = 4$ , just as is the case for  $\ell = 3$ , the isolation of the component of highest angular momentum is a nontrivial exercise [12].

### B. Perfect conductor

Based on the formalism outlined in Secs. I and II, and in Chap. 5 of Ref. [13], it is relatively straightforward to evaluate the atom-wall interaction for a perfect conductor. We first recall the known result for the atomic-dipole contribution, e.g., from Eq. (27) of Ref. [1]:

$$\mathcal{E}_1(z) = -\frac{\hbar}{16\pi^2\epsilon_0 z^3} \int_0^\infty d\omega \alpha_1(i\omega) \left[ 1 + \frac{2\omega z}{c} + 2\left(\frac{\omega z}{c}\right)^2 \right] \exp\left(-\frac{2\omega z}{c}\right). \quad (20)$$

The  $\ell = 2$  contribution to the energy shift is as follows:

$$\mathcal{E}_2(z) = -\frac{\hbar}{16\pi^2\epsilon_0 z^5} \int_0^\infty d\omega \alpha_2(i\omega) \exp\left(-\frac{2\omega z}{c}\right) \left[ \frac{3}{4} + \frac{3}{2} \frac{\omega z}{c} + \frac{4}{3} \left(\frac{\omega z}{c}\right)^2 + \frac{2}{3} \left(\frac{\omega z}{c}\right)^3 + \frac{1}{6} \left(\frac{\omega z}{c}\right)^4 \right]. \quad (21)$$

This result constitutes a correction to a result previous derived in Eq. (32) of Ref. [1]. For the octupole term, we have

$$\mathcal{E}_3(z) = -\frac{\hbar}{16\pi^2\epsilon_0 z^7} \int_0^\infty d\omega \alpha_3(i\omega) e^{-2\omega z/c} \left[ \frac{2}{3} + \frac{4}{3} \frac{\omega z}{c} + \frac{92}{75} \left(\frac{\omega z}{c}\right)^2 + \frac{152}{225} \left(\frac{\omega z}{c}\right)^3 + \frac{6}{25} \left(\frac{\omega z}{c}\right)^4 + \frac{4}{75} \left(\frac{\omega z}{c}\right)^5 + \frac{4}{675} \left(\frac{\omega z}{c}\right)^6 \right]. \quad (22)$$

For large distances, the multipole polarizabilities are suppressed by higher powers of  $z$ . Specifically, the  $2^\ell$ -pole contribution scales as  $z^{-2\ell+1}$  in the short-range limit and as  $z^{-2\ell+2}$  for  $z \rightarrow \infty$ . The general structure of the short-range asymptotic limit is given in Eq. (52), in the limit  $\epsilon(i\omega) \rightarrow \infty$ , which has the same functional dependence but a different prefactor than Eq. (49) of Ref. [1]. In the context of the current paper, it is useful to clarify that we understand by short range (see also Ref. [1]) the distance regime  $a_0 \ll z \ll a_0/\alpha$ , where  $a_0$  is the Bohr radius and  $\alpha$  is the fine-structure constant. As explained in Ref. [14], the first inequality  $a_0 \ll z$  should be taken with a grain of salt in this context; the short-range expressions derived below are actually valid down to distance regions of a few angstroms away from the surface [14,15]. From the point of view of physisorption, what we refer to as the short-range regime rather constitutes a long-range distance [14,15]. By contrast, the long-range regime as considered in the current paper refers to atom-surface distances  $z \gg a_0/\alpha$ .

Finally, on the basis of Eqs. (9) and (18), while employing, otherwise, the formalism of Ref. [1], the hexadecupole energy shift is obtained as follows:

$$\begin{aligned} \mathcal{E}_4(z) = & -\frac{\hbar}{16\pi^2\epsilon_0 z^9} \int_0^\infty d\omega \alpha_4(i\omega) e^{-2\omega z/c} \left[ \frac{5}{8} + \frac{5}{4} \frac{\omega z}{c} + \frac{115}{98} \left(\frac{\omega z}{c}\right)^2 + \frac{100}{147} \left(\frac{\omega z}{c}\right)^3 + \frac{79}{294} \left(\frac{\omega z}{c}\right)^4 + \frac{11}{147} \left(\frac{\omega z}{c}\right)^5 \right. \\ & \left. + \frac{32}{2205} \left(\frac{\omega z}{c}\right)^6 + \frac{4}{2205} \left(\frac{\omega z}{c}\right)^7 + \frac{1}{8820} \left(\frac{\omega z}{c}\right)^8 \right]. \end{aligned} \quad (23)$$

This concludes the discussion of interactions with a perfect conductor.

## III. DIELECTRIC SURFACE

### A. Dipole term

In order to analyze the multipole contributions for a dielectric, one consults the transverse electric (TE) and transverse magnetic (TM) modes given in Eqs. (18)–(20) of Ref. [1]. In this case, TE stands for incident waves whose electric field is transverse to the plane of incidence, whereas TM stands for waves whose magnetic field is transverse to the plane of incidence. The calculation is described in detail in Ref. [1]. For given wave vector  $\vec{k}$ , one has two polarization vectors, one for the TE mode, and another one for the TM mode. With these ideas in mind, it is relatively easy to rederive the following result for a dipole polarizable particle in contact

with a dielectric surface:

$$\begin{aligned} \mathcal{E}_1(z) = & -\frac{\hbar}{8\pi^2\epsilon_0 c^3} \int_0^\infty d\omega \omega^3 \alpha_1(i\omega) \\ & \times \int_1^\infty dp \exp\left(-\frac{2p\omega z}{c}\right) H(\epsilon(i\omega), p), \end{aligned} \quad (24)$$

where

$$\begin{aligned} H(\epsilon, p) = & \frac{\sqrt{\epsilon - 1 + p^2} - p}{\sqrt{\epsilon - 1 + p^2} + p} \\ & + (1 - 2p^2) \frac{\sqrt{\epsilon - 1 + p^2} - p\epsilon}{\sqrt{\epsilon - 1 + p^2} + p\epsilon}. \end{aligned} \quad (25)$$

For the convenience of the reader, a remark might be in order. Namely, in order to obtain Eq. (24) from Ref. [2], one sets, in Ref. [2],  $\epsilon_2(\omega) = 1 + N_V \alpha_1(\omega)/\epsilon_0$ , for material number 2, and one expands to first order in the volume density

$N_V = N/V$ , where  $N$  is the number of atoms and  $V$  is the volume, and one applies the principle of virtual work. This leads to the potential given in Eq. (24). The connection of Ref. [2] to the atom-surface interaction was also pointed out in Ref. [14], in Ref. [5], and in the second paragraph of p. 6 of Ref. [16]. Specifically, after the pioneering paper Ref. [2], steps toward the calculation of the long-range and short-range limits of Eq. (24) were considered in Eqs. (4.37)–(4.39) of Ref. [5], and in Eqs. (3) and (4) of Ref. [17]. The interpolating formula (24) has been given in Eqs. (18) and (21) of Ref. [18], and in Eqs. (63a) and (63b) of Ref. [1].

It is useful to investigate the function

$$K(\epsilon, z) = \int_1^\infty dp \exp\left(-\frac{2p\omega z}{c}\right) H(\epsilon, p). \quad (26)$$

For  $\epsilon \rightarrow \infty$ , we have  $H(\epsilon, p) \approx 2p^2$ , and

$$K(\epsilon, z) \stackrel{\epsilon \rightarrow \infty}{\approx} \frac{1}{2} \left(\frac{c}{z\omega}\right)^3 \left[1 + 2\frac{z\omega}{c} + 2\left(\frac{z\omega}{c}\right)^2\right], \quad (27)$$

which shows that the formula (34) is consistent with the result for the dipole interaction with a perfect conductor. For  $z \rightarrow 0$ , we have, on the other hand,

$$K(\epsilon, z) = \frac{1}{2} \left(\frac{c}{z\omega}\right)^3 \frac{\epsilon - 1}{\epsilon + 1} + \mathcal{O}(z^{-1}). \quad (28)$$

Inserting (28) into (34), we have the short-range limit as

$$\mathcal{E}_1(z) \stackrel{z \rightarrow 0}{\approx} -\frac{\hbar}{16\pi^2 \epsilon_0 z^3} \int_0^\infty d\omega \alpha_1(i\omega) \frac{\epsilon(i\omega) - 1}{\epsilon(i\omega) + 1}. \quad (29)$$

The long-range limit is obtained as a function of the static polarizability  $\alpha(0)$  and the static dielectric function  $\epsilon(0)$  as follows:

$$\mathcal{E}_1(z) \stackrel{z \rightarrow \infty}{\approx} -\frac{3c\hbar \alpha_1(0)}{32\pi^2 \epsilon_0 z^4} \Psi_1(\epsilon(0)). \quad (30)$$

Here,  $\Psi_1(\epsilon)$  is a function which is normalized to unity in the limit  $\epsilon(0) \rightarrow \infty$  (limit of a perfect conductor) and which can otherwise be expressed as follows:

$$\begin{aligned} \Psi_1(\epsilon) = & A_1(\epsilon) + B_1(\epsilon) \ln \left( \frac{\sqrt{\epsilon-1} - \sqrt{\epsilon} + 1}{\sqrt{\epsilon-1} + \sqrt{\epsilon} - 1} \right) \\ & + C_1(\epsilon) \ln \left( \frac{\sqrt{\epsilon+1} - \sqrt{\epsilon} + 1}{\sqrt{\epsilon+1} + \sqrt{\epsilon} - 1} \right). \end{aligned} \quad (31)$$

The coefficients involve both fractional and integer powers of  $\epsilon$ :

$$A_1(\epsilon) = \frac{6\epsilon^2 - 3\epsilon^{3/2} - 4\epsilon - 3\sqrt{\epsilon} + 10}{6(\epsilon - 1)}, \quad (32a)$$

$$B_1(\epsilon) = \frac{2\epsilon^3 - 4\epsilon^2 + 3\epsilon + 1}{2(\epsilon - 1)^{3/2}}, \quad (32b)$$

$$C_1(\epsilon) = -\frac{\epsilon^2}{\sqrt{\epsilon+1}}. \quad (32c)$$

The expansion about the perfect-conductor limit is

$$\Psi_1(\epsilon) = 1 - \frac{5}{4\sqrt{\epsilon}} + \frac{22}{15\epsilon} + \mathcal{O}\left(\frac{1}{\epsilon^{3/2}}\right), \quad (33)$$

which is tantamount to an expansion about a large static dielectric function  $\epsilon \equiv \epsilon(0)$ . We emphasize that the long-range limit is consistent with Eqs. (4.37)–(4.39) of Ref. [5], with Eq. (23) of Ref. [18], and with Eqs. (27)–(29) of Ref. [19].

## B. Quadrupole term

The generalization to the quadrupole polarizability reads as follows:

$$\begin{aligned} \mathcal{E}_2(z) = & -\frac{\hbar}{16\pi^2 \epsilon_0 c^5} \int_0^\infty d\omega \omega^5 \alpha_2(i\omega) \\ & \times \int_1^\infty dp e^{-2p\omega z/c} \left(\frac{p^2}{2} - \frac{1}{3}\right) H(\epsilon(i\omega), p). \end{aligned} \quad (34)$$

In the perfect conductor limit ( $\epsilon \rightarrow \infty$ ), this result is in agreement with the previously derived result given in Eq. (21). The short-range limit reads as follows:

$$\mathcal{E}_2(z) \stackrel{z \rightarrow 0}{\approx} -\frac{3\hbar}{64\pi^2 \epsilon_0 z^5} \int_0^\infty d\omega \alpha_2(i\omega) \frac{\epsilon(i\omega) - 1}{\epsilon(i\omega) + 1}. \quad (35)$$

The long-range limit is obtained as

$$\mathcal{E}_2(z) \stackrel{z \rightarrow \infty}{\approx} -\frac{35c\hbar \alpha_2(0)}{384\pi^2 \epsilon_0 z^6} \Psi_2(\epsilon(0)), \quad (36)$$

where  $\Psi_2$  has the same structure as  $\Psi_1$ :

$$\begin{aligned} \Psi_2(\epsilon) = & A_2(\epsilon) + B_2(\epsilon) \ln \left( \frac{\sqrt{\epsilon-1} - \sqrt{\epsilon} + 1}{\sqrt{\epsilon-1} + \sqrt{\epsilon} - 1} \right) \\ & + C_2(\epsilon) \ln \left( \frac{\sqrt{\epsilon+1} - \sqrt{\epsilon} + 1}{\sqrt{\epsilon+1} + \sqrt{\epsilon} - 1} \right). \end{aligned} \quad (37)$$

The coefficients are given as follows:

$$\begin{aligned} A_2(\epsilon) = & \frac{1}{140(\epsilon - 1)^2} [-120\epsilon^4 + 60\epsilon^{7/2} + 380\epsilon^3 - 180\epsilon^{5/2} \\ & - 364\epsilon^2 + 75\epsilon^{3/2} + 348\epsilon + 75\sqrt{\epsilon} - 224], \end{aligned} \quad (38a)$$

$$B_2(\epsilon) = \frac{3}{28} \frac{8\epsilon^5 - 28\epsilon^4 + 40\epsilon^3 - 34\epsilon^2 + 7\epsilon + 5}{(\epsilon - 1)^{5/2}}, \quad (38b)$$

$$C_2(\epsilon) = \frac{3}{7} \frac{\epsilon^2(2\epsilon - 1)}{\sqrt{\epsilon+1}}. \quad (38c)$$

The expansion about the perfect-conductor limit is

$$\Psi_2(\epsilon) = 1 - \frac{31}{28\sqrt{\epsilon}} + \frac{338}{245\epsilon} + \mathcal{O}\left(\frac{1}{\epsilon^{3/2}}\right). \quad (39)$$

### C. Octupole term

For the interaction with a dielectric surface, the octupole energy shift reads as follows:

$$\mathcal{E}_3(z) = -\frac{\hbar}{16\pi^2 \epsilon_0 c^7} \int_0^\infty d\omega \omega^7 \alpha_3(i\omega) \int_1^\infty dp e^{-2p\omega z/c} \left( \frac{8}{135} p^4 - \frac{16}{225} p^2 + \frac{4}{225} \right) H(\epsilon(i\omega), p). \quad (40)$$

The calculation of the dielectric response function for imaginary input frequencies is a nontrivial problem. The short-range limit is given by the expression

$$\mathcal{E}_3(z) \stackrel{z \rightarrow 0}{\approx} -\frac{\hbar}{24\pi^2 \epsilon_0 z^7} \int_0^\infty d\omega \alpha_3(i\omega) \frac{\epsilon(i\omega) - 1}{\epsilon(i\omega) + 1}. \quad (41)$$

The long-range limit is

$$\mathcal{E}_3(z) \stackrel{z \rightarrow \infty}{\approx} -\frac{77c\hbar \alpha_3(0)}{800\pi^2 \epsilon_0 z^8} \Psi_3(\epsilon(0)), \quad (42)$$

where  $\Psi_3$  reads as follows:

$$\Psi_3(\epsilon) = A_3(\epsilon) + B_3(\epsilon) \ln \left( \frac{\sqrt{\epsilon-1} - \sqrt{\epsilon+1}}{\sqrt{\epsilon-1} + \sqrt{\epsilon-1}} \right) + C_3(\epsilon) \ln \left( \frac{\sqrt{\epsilon+1} - \sqrt{\epsilon+1}}{\sqrt{\epsilon+1} + \sqrt{\epsilon-1}} \right). \quad (43)$$

The coefficients are given as follows:

$$A_3(\epsilon) = \frac{1}{11088(\epsilon-1)^3} \left[ -2520\epsilon^{11/2} - 28560\epsilon^5 + 13860\epsilon^{9/2} + 66528\epsilon^4 - 31290\epsilon^{7/2} - 76336\epsilon^3 + 29120\epsilon^{5/2} + 62016\epsilon^2 - 2415\epsilon^{3/2} - 48675\epsilon - 6195\sqrt{\epsilon} + 19888 \right], \quad (44a)$$

$$B_3(\epsilon) = \frac{5}{528(\epsilon-1)^{7/2}} [48\epsilon^7 - 288\epsilon^6 + 712\epsilon^5 - 976\epsilon^4 + 890\epsilon^3 - 444\epsilon^2 + 5\epsilon + 59], \quad (44b)$$

$$C_3(\epsilon) = -\frac{5}{33} \frac{3\epsilon^2 - 6\epsilon + 1}{\sqrt{\epsilon+1}}. \quad (44c)$$

The expansion about the perfect-conductor limit is

$$\Psi_3(\epsilon) = 1 - \frac{265}{264\sqrt{\epsilon}} + \frac{914}{693\epsilon} + \mathcal{O}\left(\frac{1}{\epsilon^{3/2}}\right). \quad (45)$$

### D. Hexadecupole term

For the interaction with a dielectric surface, the octupole energy shift reads as follows:

$$\mathcal{E}_4(z) = -\frac{\hbar}{16\pi^2 \epsilon_0 c^9} \int_0^\infty d\omega \omega^9 \alpha_4(i\omega) \int_1^\infty dp e^{-2p\omega z/c} \left( \frac{1}{252} p^6 - \frac{1}{147} p^4 + \frac{1}{294} p^2 - \frac{1}{2205} \right) H(\epsilon(i\omega), p). \quad (46)$$

The short-range limit is

$$\mathcal{E}_4(z) \stackrel{z \rightarrow 0}{\approx} -\frac{5\hbar}{128\pi^2 \epsilon_0 z^9} \int_0^\infty d\omega \alpha_4(i\omega) \frac{\epsilon(i\omega) - 1}{\epsilon(i\omega) + 1}. \quad (47)$$

The long-range limit is obtained as

$$\mathcal{E}_4(z) \stackrel{z \rightarrow \infty}{\approx} -\frac{1287c\hbar \alpha_4(0)}{12544\pi^2 \epsilon_0 z^{10}} \Psi_4(\epsilon(0)), \quad (48)$$

where  $\Psi_4$  reads as follows:

$$\Psi_4(\epsilon) = A_4(\epsilon) + B_4(\epsilon) \ln \left( \frac{\sqrt{\epsilon-1} - \sqrt{\epsilon+1}}{\sqrt{\epsilon-1} + \sqrt{\epsilon-1}} \right) + C_4(\epsilon) \ln \left( \frac{\sqrt{\epsilon+1} - \sqrt{\epsilon+1}}{\sqrt{\epsilon+1} + \sqrt{\epsilon-1}} \right). \quad (49)$$

The coefficients are given as follows:

$$A_4(\epsilon) = \frac{1}{205\,920(\epsilon - 1)^4} \left[ -40\,320\epsilon^8 + 20\,160\epsilon^{15/2} + 369\,600\epsilon^7 - 181\,440\epsilon^{13/2} - 1\,338\,624\epsilon^6 + 641\,760\epsilon^{11/2} \right. \\ \left. + 2\,670\,816\epsilon^5 - 1\,252\,440\epsilon^{9/2} - 3\,242\,464\epsilon^4 + 1\,409\,520\epsilon^{7/2} + 2\,767\,936\epsilon^3 - 690\,270\epsilon^{5/2} - 2\,110\,464\epsilon^2 \right. \\ \left. - 62\,265\epsilon^{3/2} + 1\,300\,000\epsilon + 118\,125\epsilon^{1/2} - 376\,480 \right], \quad (50a)$$

$$B_4(\epsilon) = -\frac{7}{4576(\epsilon - 1)^{9/2}} [128\epsilon^9 - 1216\epsilon^8 + 4608\epsilon^7 - 9600\epsilon^6 + 12\,720\epsilon^5 - 12\,120\epsilon^4 + 8080\epsilon^3 - 2580\epsilon^2 - 405\epsilon + 375], \quad (50b)$$

$$C_4(\epsilon) = \frac{7}{143} \frac{4\epsilon^3 - 18\epsilon^2 + 12\epsilon - 1}{\sqrt{\epsilon + 1}}. \quad (50c)$$

The expansion about the perfect-conductor limit is

$$\Psi_4(\epsilon) = 1 - \frac{1323}{1430\sqrt{\epsilon}} + \frac{18\,050}{14\,157\epsilon} + \mathcal{O}\left(\frac{1}{\epsilon^{3/2}}\right). \quad (51)$$

### E. Some general short-range results

In the short-range limit, a few simplifications and generalizations are possible, especially in regard to two-body bound systems like hydrogen and positronium. First, we may point out the generalization of the short-range expressions given in Eqs. (29), (35), (41), and (47), to arbitrary multipole orders. Indeed, the general result for the  $2^\ell$ -pole effect reads as follows:

$$\mathcal{E}_\ell(z) \stackrel{z \rightarrow 0}{\equiv} -\frac{\hbar}{16\pi^2 \epsilon_0 z^{2\ell+1}} \frac{\ell + 1}{2\ell} \int_0^\infty d\omega \alpha_\ell(i\omega) \frac{\epsilon(i\omega) - 1}{\epsilon(i\omega) + 1}. \quad (52)$$

This result has the same functional form as Eq. (49) of Ref. [1], but a different, updated prefactor.

## IV. CALCULATION OF MULTIPOLE CORRECTIONS

### A. Multipoles for hydrogen and positronium

We aim to give an update on multipole corrections to atom-surface interactions, beyond the discussion in Ref. [1]. Hydrogen and positronium constitute atomic systems for which the exact evaluation of multipole polarizabilities is possible analytically (see the Appendix). Hence, we focus on these two atomic systems, for definiteness, while stressing that other atomic systems could be more interesting from the point of view of applications (see Sec. IV C). The derivation of the multipole polarizabilities of hydrogen and positronium uses the Sturmian decomposition of the Schrödinger-Coulomb Green function, and the evaluation of radial matrix elements, according to the formalism outlined in Chap. 4 of Ref. [13]. In order to ensure concise formulas, we now switch to atomic units (see Chap. 2 of Ref. [13]) with  $a_0 = 1$ ,  $E_h = 1$ ,  $\epsilon_0 = 1/(4\pi)$ ,  $\hbar = 1$ , and  $e = 1$  (unit elementary charge).

Using the results given in the Appendix, we are now in the position to derive some more closed-form expressions for interactions with a perfect conductor, i.e., in the limit  $\epsilon(i\omega) \rightarrow \infty$ . Specifically, for multipole interactions with atomic hydro-

gen, one obtains the following result for the integral over the  $2^\ell$ -pole polarizability:

$$\int_0^\infty d\omega \alpha_\ell(i\omega) = \frac{\pi \Gamma(2\ell + 3)}{2^{2\ell+1} (2\ell + 1)} \frac{a_0^{2\ell}}{\hbar}. \quad (53)$$

The general result for the  $2^\ell$ -pole energy shift for hydrogen interacting with a perfect conductor thus is as follows:

$$\mathcal{E}_\ell^{(H)}(z) \stackrel{z \rightarrow 0, \epsilon \rightarrow \infty}{\equiv} -\frac{(\ell + 1) \Gamma(2\ell + 3)}{2^{2\ell+4} \ell (2\ell + 1)} \frac{E_h}{(z/a_0)^{2\ell+1}}. \quad (54)$$

Here,  $E_h$  is the Hartree energy, and  $a_0$  is the Bohr radius. The ratio  $z/a_0$  is equal to the atom-wall distance, expressed in atomic units (see Chap. 2 of Ref. [13]). For positronium, one obtains the result

$$\mathcal{E}_\ell^{(Ps)}(z) \stackrel{z \rightarrow 0, \epsilon \rightarrow \infty}{\equiv} -\frac{(\ell + 1) \Gamma(2\ell + 3)}{16 \ell (2\ell + 1)} \frac{E_h}{(z/a_0)^{2\ell+1}}. \quad (55)$$

In the short-range regime, the expansion into multipoles constitutes an expansion in powers of  $a_0/z$ , where  $a_0$  is the Bohr radius and  $z$  is the atom-wall distance.

The general results given in Eqs. (54) and (55) demonstrate that the sum over the multipole potentials (at least for hydrogen and positronium interacting with a perfect conductor) constitutes a divergent, asymptotic series. The divergence, for any distance  $z$ , happens due to the factorial growth of the prefactor  $\Gamma(2\ell + 3)$ . Optimal truncation of the multipole expansion at the smallest term of the series then constitutes a valid procedure for obtaining theoretical predictions [21], while Borel summation can be used in order to sum the divergent series [22].

### B. Hydrogen, positronium, and $\alpha$ -quartz

We aim to combine the analysis of the multipole polarizabilities given in the Appendix and Sec. IV A with an update on  $\alpha$ -quartz [1]. For the data presented in Ref. [20], we used

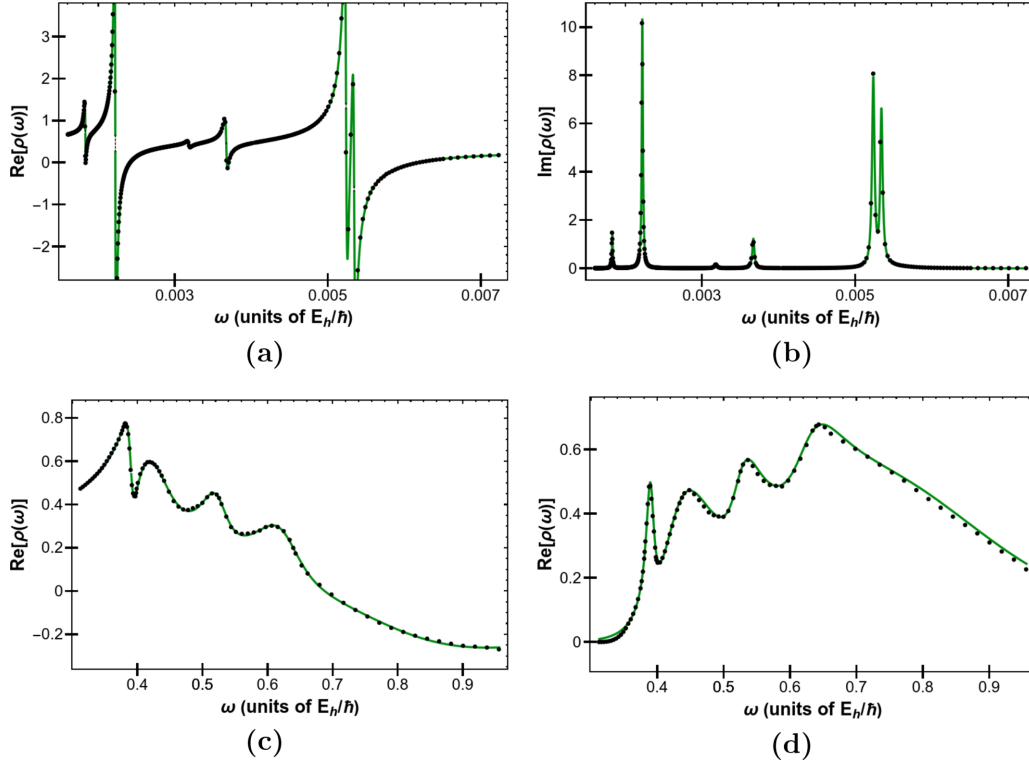


FIG. 1. A reanalysis of the dielectric function of  $\alpha$ -quartz (ordinary axis) is performed based on Eq. (58), with fitting parameters given in Table I. The angular frequency is measured in atomic units, i.e., in units of  $E_h/\hbar$ , where  $E_h$  is the Hartree energy and  $\hbar$  is the reduced Planck constant. The panels refer to the (a) lattice resonance region, real part of  $\rho(\omega)$ ; (b) lattice resonance region, imaginary part of  $\rho(\omega)$ ; (c) interband region, real part of  $\rho(\omega)$ ; and (d) interband region, imaginary part of  $\rho(\omega)$ . The data points are taken from Ref. [20], while the solid curve is described by Eq. (58), with parameters given in Table I.

the following fit formula discussed in Ref. [1]:

$$\begin{aligned} \rho(\omega) &\equiv \frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 2} = \frac{[n(\omega) + i k(\omega)]^2 - 1}{[n(\omega) + i k(\omega)]^2 + 2} \\ &\simeq \sum_{k=1}^n \frac{\alpha_k \omega_k^2}{\omega_k^2 - i \gamma_k \omega - \omega^2}. \end{aligned} \quad (56)$$

Here,  $n(\omega)$  and  $k(\omega)$  are the dispersive and absorptive parts of the index of refraction, while the functional form is inspired by the Clausius-Mossotti equation. We take the opportunity to point out the missing factor  $\omega_k^2$  in the numerator of the fitting function given in Eq. (70) of Ref. [1]. The missing prefactor had previously been supplemented in Eq. (21) of Ref. [23]. For completeness, it might be useful to point out that the expression  $[\epsilon(\omega) - 1]/[\epsilon(\omega) + 1]$ , which appears in the integrand of the short-range expressions (29), (35), (41), and (47), can be obtained from  $\rho(\omega)$  as follows:

$$\frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 1} = \frac{3\rho(\omega)}{\rho(\omega) + 2}. \quad (57)$$

For intrinsic silicon [19], we have recently found that a better analytic representation can be obtained based on the following fit formula:

$$\rho(\omega) \simeq \sum_{k=1}^n \frac{\alpha_k (\omega_k^2 - i \gamma_k' \omega)}{\omega_k^2 - i \gamma_k \omega - \omega^2} \quad (58)$$

where the expression  $[\alpha_k (\omega_k^2 - i \gamma_k' \omega)]$  can be regarded as a complex oscillator strength that includes a phenomenological model of radiative reaction [19]. We find that such a model represents the data from Ref. [20] very well (see Figs. 1 and 2, as well as Table I). This finding is nontrivial in view of the necessity for any fit function to fulfill the Kramers-Kronig relationships (see, e.g., Chap. 6 of Ref. [24]), which relate the real and imaginary parts of  $\rho$  and  $\epsilon$ . The functional form of our model (58) fulfills the Kramers-Kronig relationships automatically. While the oscillator strengths and resonance frequencies for vibrational excitations differ in between the ordinary and the extraordinary axis of  $\alpha$ -quartz (see Table I), we find that the influence of the low-frequency vibrational excitations on the leading short-range expansion coefficients reported below is numerically negligible. Similar approaches as described by Eq. (58) have been discussed (for rutile) in Eq. (1) of Ref. [25], in Eq. (4) of Ref. [26] (for cubic thallium), in Eq. (1) of Ref. [27] (for sodium nitrate), and in Eq. (5) of Ref. [28] (for orthorhombic sulfur).

We are now in the position to analyze the multipole corrections for  $\alpha$ -quartz. In general, we can say that these intriguing corrections to atom-surface interactions have generated considerable interest [see, e.g., Ref. [29], Eq. (2) of Ref. [15], and Eq. (8) of Ref. [30]]. In order to put this finding into perspective, we should point out that it has recently become possible to calculate the multipole corrections to polarizabilities more accurately from first principles, for general multielectron atoms [31]. In this paper, in



TABLE I. We indicate the coefficients for the first few resonances for  $\alpha$ -quartz according to the fitting formula (58), for the ordinary and the extraordinary optical axis. The values for  $\omega_k$ ,  $\gamma_k$ , and  $\gamma'_k$  are measured in atomic units, i.e., in units of  $E_h/\hbar$ . The subscript  $k$  numbers the resonances.

$k$	$\alpha_k$	$\omega_k$	$\gamma_k$	$\gamma'_k$
Ordinary axis: Vibrational excitations				
1	$1.045 \times 10^{-2}$	$1.827 \times 10^{-3}$	$1.301 \times 10^{-5}$	$1.631 \times 10^{-5}$
2	$8.541 \times 10^{-2}$	$2.218 \times 10^{-3}$	$1.835 \times 10^{-5}$	$-1.528 \times 10^{-6}$
3	$2.022 \times 10^{-3}$	$3.180 \times 10^{-3}$	$4.026 \times 10^{-5}$	$1.019 \times 10^{-4}$
4	$1.111 \times 10^{-2}$	$3.668 \times 10^{-3}$	$3.381 \times 10^{-5}$	$3.423 \times 10^{-5}$
5	$5.850 \times 10^{-2}$	$5.234 \times 10^{-3}$	$3.959 \times 10^{-5}$	$-3.881 \times 10^{-5}$
6	$4.472 \times 10^{-2}$	$5.339 \times 10^{-3}$	$3.776 \times 10^{-5}$	$4.041 \times 10^{-4}$
Ordinary axis: Interband excitations				
7	$1.341 \times 10^{-2}$	$3.899 \times 10^{-1}$	$1.423 \times 10^{-2}$	$-1.195 \times 10^{-1}$
8	$8.086 \times 10^{-2}$	$4.287 \times 10^{-1}$	$9.996 \times 10^{-2}$	$4.432 \times 10^{-1}$
9	$1.568 \times 10^{-2}$	$5.245 \times 10^{-1}$	$5.322 \times 10^{-2}$	$7.333 \times 10^{-1}$
10	$2.520 \times 10^{-1}$	$6.270 \times 10^{-1}$	$9.280 \times 10^{-2}$	$8.041 \times 10^{-1}$
11	$1.772 \times 10^{-1}$	$8.237 \times 10^{-1}$	$4.981 \times 10^{-1}$	$-4.361 \times 10^{-1}$
Extraordinary axis: Vibrational excitations				
1	$3.628 \times 10^{-2}$	$1.736 \times 10^{-3}$	$2.316 \times 10^{-5}$	$2.316 \times 10^{-5}$
2	$6.734 \times 10^{-2}$	$2.418 \times 10^{-3}$	$2.811 \times 10^{-5}$	$4.267 \times 10^{-5}$
3	$1.023 \times 10^{-2}$	$2.430 \times 10^{-3}$	$9.981 \times 10^{-5}$	$-3.154 \times 10^{-3}$
4	$1.114 \times 10^{-2}$	$3.578 \times 10^{-3}$	$3.594 \times 10^{-5}$	$2.118 \times 10^{-3}$
5	$1.026 \times 10^{-1}$	$5.307 \times 10^{-3}$	$4.383 \times 10^{-5}$	$2.533 \times 10^{-4}$
Extraordinary axis: Interband excitations				
6	$1.351 \times 10^{-2}$	$3.899 \times 10^{-1}$	$1.428 \times 10^{-2}$	$-1.172 \times 10^{-1}$
7	$7.775 \times 10^{-2}$	$4.283 \times 10^{-1}$	$9.861 \times 10^{-2}$	$4.422 \times 10^{-1}$
8	$1.512 \times 10^{-2}$	$5.245 \times 10^{-1}$	$5.229 \times 10^{-2}$	$7.323 \times 10^{-1}$
9	$2.430 \times 10^{-1}$	$6.272 \times 10^{-1}$	$9.108 \times 10^{-2}$	$7.971 \times 10^{-1}$
10	$1.859 \times 10^{-1}$	$8.209 \times 10^{-1}$	$5.049 \times 10^{-1}$	$-4.160 \times 10^{-1}$

order to facilitate the analysis of the multipole corrections, we have evaluated exact expressions for hydrogen and positronium up to the hexadecupole order (see the Appendix and Sec. IV A).

It is indicated to include a brief discussion on the magnitude of the multipole corrections. We continue to use atomic units. *A priori*, the short-range approximations are valid for  $z \leq 1/\alpha \approx 137.036$  in atomic units, i.e., for distances smaller than about 137 Bohr radii [1,32]. The upper end of the range of validity of the short-range, nonretarded approximation and its dependence on the atomic species has recently been discussed in Ref. [33]. The leading term for the  $2^\ell$ -pole multipole term is proportional to  $1/z^{2\ell+1}$ . It is well known that Lifshitz theory cannot be used for arbitrarily close approach to the surface. The probability density of atomic wave functions (for ground-state hydrogen atoms) decreases with a probability  $|\psi|^2 \sim \exp(-2r)$ , where  $r$  is the distance from the nucleus in atomic units. For a distance of  $z = 0.5$  nm, which is roughly equal to  $z = 10$  in atomic units, one has  $|\psi|^2 \sim 10^{-9}$ , eliminating the overlap as a possible limiting factor. It has been stressed in Ref. [14] that, for vanishing overlap of the atomic wave function with the surface, the exchange of electrons between the atom and the substrate can be neglected, which, in turn, makes it possible to treat the electrons (and nuclei) of the atom and the surface as distinguishable. Furthermore, in the seminal paper Ref. [14], it has been stressed in remarks following Eq. (2.39) that even

for separations typically encountered in physisorption ( $\approx 4$ – $7$  Bohr radii) the formula  $V(z) \approx -C_3/(z - z_0)^3$  is applicable. Here,  $C_3$  is given implicitly in Eq. (29). Here,  $z_0$  is the position of a suitably defined reference plane given by Eq. (2.38) of Ref. [14]. The position of the reference plane (see also Fig. 1 of Ref. [14]) is given by an integral which depends on both the susceptibility of the atom and also [via the integral given in Eq. (2.28) of Ref. [14]] the susceptibility of the solid. One accepted path toward the calculation of physisorption energies has involved the addition of an ultrashort-range (overlap) contribution to the energy, which is calculated on the basis of density-functional (DFT) theory, and the van der Waals energy, the latter being calculated according to the ideas outlined in Ref. [14]. One possible pathway toward the calculation of the contact contribution (the DFT part) is based on DFT-GGA, where GGA stands for the generalized gradient approximation [34]. The entire procedure is often referred to as the van der Waals corrected DFT approach [35–38]. A calculation of the reference-plane position  $z_0$  for  $\alpha$ -quartz is beyond the scope of the current paper. We merely use an exemplary distance of  $z = 10$  a.u. for the calculations reported below, in order to illustrate the magnitude of the multipole corrections for close approach, and furthermore, assume positronium to be at rest (see Refs. [39,40]).

We can thus use an exemplary distance of  $z = 10$  a.u., in order to analyze the magnitude of the multipole corrections. A further remark is in order. It has recently been shown in

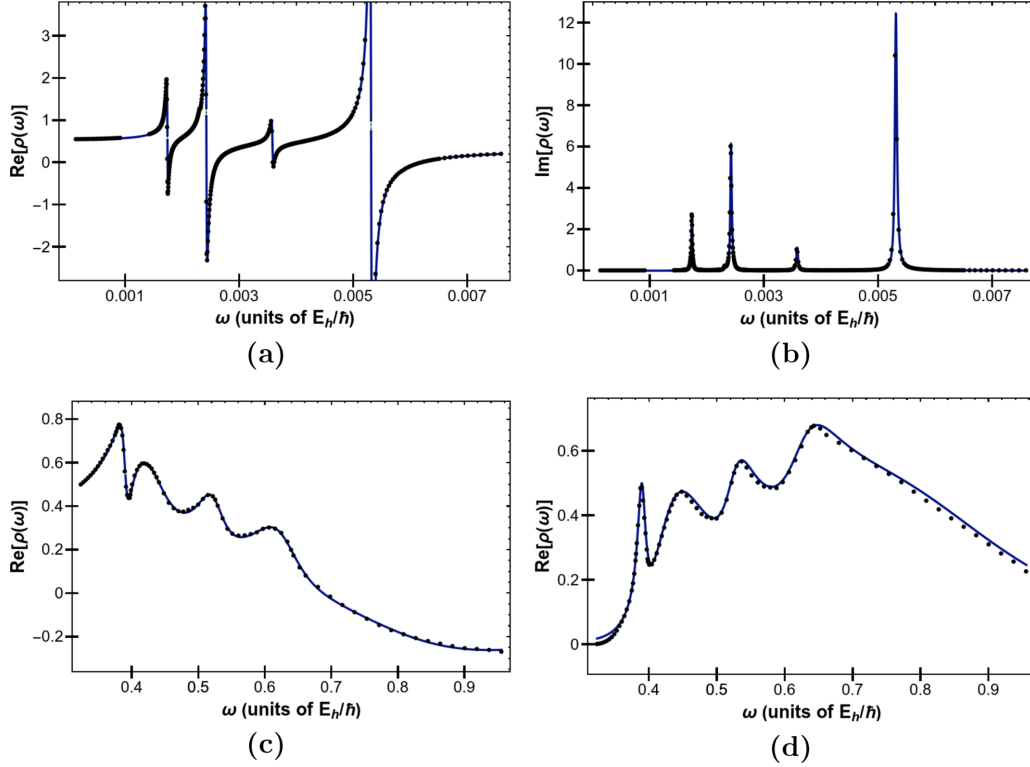


FIG. 2. We present the analog of Fig. 1, but for the extraordinary axis. Specifically, the dielectric function of  $\alpha$ -quartz (extraordinary axis) is analyzed based on Eq. (58), with fitting parameters given in Table I. The angular frequency is measured in atomic units, i.e., in units of  $E_h/\hbar$ , where  $E_h$  is the Hartree energy and  $\hbar$  is the reduced Planck constant. The panels refer to the (a) lattice resonance region, real part of  $\rho(\omega)$ ; (b) lattice resonance region, imaginary part of  $\rho(\omega)$ ; (c) interband region, real part of  $\rho(\omega)$ ; and (d) interband region, imaginary part of  $\rho(\omega)$ . The data points are taken from Ref. [20], while the solid curve is described by Eq. (58), with parameters given in Table I.

Ref. [32] that higher-order terms in the atom-surface potential contain logarithms of the atom-wall distance,  $\ln(z)$ , leading to a semianalytic expansion of the atom-surface potential in powers of  $z$  and  $\ln(z)$ , described by coefficients with two indices. Hence, we will refer to the leading short-range coefficient multiplying for the atom-surface dipole and quadrupole terms as  $C_{30}$  and  $C_{50}$  (rather than  $C_3$  and  $C_5$ ), where the first index counts the power of  $z$  and the second index (equal to zero) indicates the absence of a logarithm [32].

For a perfect conductor, we thus write the relations

$$\mathcal{E}_1(z) \approx -\frac{C_{30}}{z^3}, \quad \mathcal{E}_2(z) \approx -\frac{C_{50}}{z^5}, \quad 1 \ll z \ll \alpha^{-1}, \quad (59)$$

with the following exemplary results (for the dipole and quadrupole coefficients) for perfect conductors [see Eqs. (54) and (55)]:

$$C_{30}^{(\text{H})} \stackrel{\epsilon \rightarrow \infty}{=} \frac{1}{4}, \quad C_{50}^{(\text{H})} \stackrel{\epsilon \rightarrow \infty}{=} \frac{27}{32}, \quad (60)$$

$$C_{30}^{(\text{Ps})} \stackrel{\epsilon \rightarrow \infty}{=} 1, \quad C_{50}^{(\text{Ps})} \stackrel{\epsilon \rightarrow \infty}{=} \frac{27}{2}. \quad (61)$$

For  $\alpha$ -quartz, we refer to Tables II and III for the multipole coefficients. For positronium, at  $z = 10$  a.u., one has the following ratio of the quadrupole corrections to the leading dipole term:

$$\frac{\mathcal{E}_2^{(\text{Ps})}(z = 10)}{\mathcal{E}_1^{(\text{Ps})}(z = 10)} = \frac{C_{50}^{(\text{Ps})}}{C_{30}^{(\text{Ps})} \times (10)^2} = \begin{cases} 0.135 & (\text{conductor}) \\ 0.124 & (\alpha\text{-quartz}) \end{cases}. \quad (62)$$

A deviation by 13.5% is larger than the uncertainty of many current measurements of the dielectric function of materials [41]. For hydrogen, the quadrupole correction is

$$\begin{aligned} \frac{\mathcal{E}_2^{(\text{H})}(z = 10)}{\mathcal{E}_1^{(\text{H})}(z = 10)} &= \frac{C_{50}^{(\text{H})}}{C_{30}^{(\text{H})} \times (10)^2} \\ &= \begin{cases} 0.0336 & (\text{conductor}) \\ 0.0296 & (\alpha\text{-quartz}) \end{cases}, \quad (63) \end{aligned}$$

which is of the order of a few percent. These observations are consistent with the literature [15]. In the study of atom-wall interactions, atomic systems with an exceptionally large static polarizability have attracted considerable attention. One example is metastable helium (in the metastable spin-triplet state) with a static polarizability of 315 a.u. (see Ref. [42]). For such systems, one can expect even larger corrections due

TABLE II. Coefficient  $C_{(2\ell+1)0}$  multiplying the leading term for the  $2^\ell$ -pole contribution to the atom-surface interaction given in atomic units, for hydrogen interacting with a (perfect) conductor, and with  $\alpha$ -quartz.

	$C_{(2\ell+1)0}$ for hydrogen			
	$\ell = 1$	$\ell = 2$	$\ell = 3$	$\ell = 4$
Conductor	0.250	0.844	7.50	123
$\alpha$ -quartz	0.0599	0.178	1.48	23.4

TABLE III. Same as Table II for positronium.

	$C_{(2\ell+1)0}$ for positronium			
	$\ell = 1$	$\ell = 2$	$\ell = 3$	$\ell = 4$
Conductor	1.00	13.5	480	31500
$\alpha$ -quartz	0.302	3.73	127	8130

to quadrupole effects. Investigations in these directions are currently in progress. In the current section, we restrict our attention to hydrogen and positronium, for which the multipole polarizabilities can be evaluated in closed analytic form (see the Appendix).

### C. Applications to physisorption

As already outlined above, the application of van der Waals corrected density-functional theory to the adsorption of rare gases on surfaces is a standard process in surface physics [14,34–37,43]. In this context, one adds the van der Waals energy which is due to the interaction with all atoms in the solid, evaluated at the adsorption coordinate, to a DFT term, which results from the interaction with the nearest neighbors at the adsorption site. This approach had been mentioned in the text in the upper right column of p. 2280 of Ref. [14]. The method has been further developed over a couple of decades; the justification for this approach and the general theoretical background are discussed in Refs. [14,15,34–38,43,44].

One of the most important results of the current paper is the additional factor  $(\ell + 1)/(2\ell)$  in Eq. (54) as compared to the results communicated in Ref. [1]. This correction factor evaluates to 3/4 for the quadrupole term. This correction factor also affects a few results recorded in the literature, for example, the  $C_5$  coefficients reported in Ref. [31]. In Ref. [14], the authors take into account the effect of the reference plane at  $z_0$  in the modified expansion

$$V(z) = -\frac{C_3}{(z - z_0)^3} - \frac{C'_5}{(z - z_0)^5} - \dots, \quad (64)$$

where  $C'_5 = C_5 + 6C_3z_0^2$ , and  $C_5$  is the quadrupole coefficient from Eq. (54), which reads as follows (in atomic units):

$$C_5 = \frac{3}{16\pi} \int_0^\infty d\omega \alpha_2(i\omega) \frac{\epsilon(i\omega) - 1}{\epsilon(i\omega) + 1}. \quad (65)$$

Let us consider two examples taken from Table III of Ref. [15], namely, Kr on Cu(111) and Ar on Pd(111). For Kr on Cu(111), one has  $C_3 = 0.558$  and  $C'_5 = 3.963$  in atomic units according to Table III of Ref. [15], as well as  $z_{\text{eq}} = 5.99$  (equilibrium position) and  $z_0 = 0.39$ . One can easily solve for  $C_5 = 3.453$  (before correction) and  $C_5 = 2.590$  (after correction with the multiplicative factor 3/4). Adding the result from DFT-GGA from Table III of Ref. [15], which is 20.3 meV, one obtains the modified van der Waals corrected adsorption energy of 121 meV which is even closer to the value of 119 meV from Ref. [38] than the value of 126 meV given in Table III of Ref. [15].

For Ar on Pd(111), one has  $C_3 = 0.476$  and  $C'_5 = 2.584$  in atomic units according to Table III of Ref. [15], as well as  $z_{\text{eq}} = 5.59$  (equilibrium position) and  $z_0 = 0.26$ . One then

solves for  $C_5 = 2.391$  (before correction) and  $C_5 = 1.793$  (after correction). Adding the result for DFT-GGA from Table III of Ref. [15], which is 14.9 meV, one obtains the modified van der Waals corrected adsorption energy of 113 meV which is a bit closer to the comparison value of 110 meV from Ref. [43] than the value of 117 meV originally given in Table III of Ref. [15]. Further considerations on adsorption energies are currently in progress.

## V. CONCLUSIONS

In this paper, we have (re)derived (see Ref. [1]) the quadrupole, octupole, and hexadecupole corrections to the atom-wall interaction, with a special emphasis on the isolation of the relevant angular momentum components from the derivative tensors of the electric field. The functional form of our results is the same as the one obtained in Ref. [1], but important differences are obtained for the prefactors.

The general results for the dipole, quadrupole, octupole, and hexadecupole contributions to the atom-wall interactions have been given in Eqs. (24), (34), (40), and (46), respectively. Short-range limits have been given for either term in Eqs. (29), (35), (41), and (47), and the long-range limits have been analyzed in Eqs. (30), (36), (42), and (48). For the long-range limit, we have found rather concise formulas for the dependence of the coefficient multiplying the term proportional to  $z^{-2\ell-2}$ , in terms of logarithms [see Eqs. (31), (37), (43), and (49)]. The analytic results for the long-range limit constitute an important addition to the results originally reported in Ref. [1].

Furthermore, we find that the expansion into multipole terms constitutes an asymptotic, divergent series [see Eqs. (54) and (55)]. Series with factorially divergent coefficients can, in many cases, be summed using generalizations of the Borel method [21,22]. Furthermore, a truncation of the series at the smallest term yields an excellent approximation to the complete result, so that the divergent character of the series is not an obstacle to the deduction of theoretical predictions. We find that it is possible to express the quadrupole, octupole, and hexadecupole polarizabilities of hydrogen and positronium in closed analytic form (see the Appendix). This enables us to reanalyze multipole corrections, with a special emphasis on hydrogen and positronium. We find that the quadrupole correction is phenomenologically relevant [see Eqs. (62) and (63)]. A concrete application is discussed in Sec. IV C. A reanalysis of the dielectric function of  $\alpha$ -quartz using the functional form given in Eq. (58) reveals very good agreement with numerical data from Ref. [20]. For the short-range coefficients of the multipole corrections to the atom-surface interactions (perfect conductor and  $\alpha$ -quartz), we present results in Tables II and III. These data confirm the rapid growth of the coefficients multiplying the multipole corrections, both for interactions with perfect conductor and  $\alpha$ -quartz, consistent with the eventual factorial divergence of the series. Applications to physisorption (van der Waals corrected density-functional theory) are discussed in Sec. IV C. The modified result for the quadrupole correction derived here yields important corrections to results previously communicated in Ref. [15].

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### APPENDIX: MULTIPOLE POLARIZABILITIES OF HYDROGEN AND POSITRONIUM

Hydrogen and positronium constitute atomic systems for which the exact evaluation of multipole polarizabilities is possible analytically. Hence, we focus on these two atomic systems, for definiteness, while stressing that other atomic systems could be more interesting from the point of view of applications (see Sec. IV C). In this Appendix, we use atomic units (see Chap. 2 of Ref. [13]) with  $a_0 = 1$ ,  $E_h = 1$ ,  $\epsilon_0 = 1/(4\pi)$ ,  $\hbar = 1$  and  $e = 1$  (unit elementary charge). The atoms of interest are hydrogen and positronium. With techniques outlined in Ref. [45] and in Chap. 4 of Ref. [13], it is possible to derive closed-form expressions for hydrogen and positronium which we use in the nonrelativistic and nonrecoil limit. We consider the specialization of the tensor (11) to a one-electron atom and work with the matrix element

$$Q_\ell^{(\text{H})}(\omega) = \frac{1}{2\ell + 1} \sum_m \left\langle Q_{\ell m} \frac{1}{H - E_{1S}^{(\text{H})} + \omega} Q_{\ell m}^* \right\rangle_{1S}, \quad (\text{A1})$$

where the superscript indicates the atom (H stands for hydrogen). From  $Q_\ell^{(\text{H})}(\omega)$ , one obtains the  $2^\ell$ -pole polarizability as follows:

$$\alpha_\ell^{(\text{H})}(\omega) = Q_\ell^{(\text{H})}(\omega) + Q_\ell^{(\text{H})}(-\omega). \quad (\text{A2})$$

The polarizability of positronium can be obtained from the hydrogen result as follows:

$$\alpha_\ell^{(\text{Ps})}(\omega) = 2^{2\ell+1} [Q_\ell^{(\text{H})}(2\omega) + Q_\ell^{(\text{H})}(-2\omega)]. \quad (\text{A3})$$

According to Eq. (4.154) of Ref. [13], the dipole term can be expressed in terms of a variable  $t$ ,

$$Q_1^{(\text{H})}(\omega) = \frac{2t^2 p^{(1)}(t)}{3(1-t)^5(1+t)^4} + \frac{256t^9 f(t)}{3(1+t)^5(1-t)^5}, \quad (\text{A4})$$

where the photon energy is parametrized by the  $t$  variable:

$$t = t(\omega) = \frac{1}{\sqrt{1+2\omega}}. \quad (\text{A5})$$

The polynomial  $p^{(1)}(t)$  incurred in Eq. (A4) is

$$p^{(1)}(t) = 3 - 3t - 12t^2 + 12t^3 + 19t^4 - 19t^5 - 26t^6 - 38t^7. \quad (\text{A6})$$

Within the representation in terms of the  $t$  variable, the transition to positronium amounts to the replacement  $t \rightarrow t'$  where  $t' = t'(\omega) = (1+4\omega)^{-1/2}$ . The quadrupole term reads as follows:

$$Q_2^{(\text{H})}(\omega) = \frac{t^2 p^{(2)}(t)}{5(1-t)^7(1+t)^6} - \frac{4096t^{11}(t^2-4)f(t)}{5(t^2-1)^7}. \quad (\text{A7})$$

The polynomial  $p^{(2)}(t)$  reads as follows:

$$p^{(2)}(t) = 45 - 45t - 285t^2 + 285t^3 + 786t^4 - 786t^5 - 1322t^6 + 1322t^7 + 2865t^8 + 5327t^9 - 553t^{10} - 1495t^{11}. \quad (\text{A8})$$

The octupole term is

$$Q_3^{(\text{H})}(\omega) = \frac{9t^2 p^{(3)}(t)}{7(1-t)^9(1+t)^8} - \frac{36864t^{13}(t^2-4)(t^2-9)f(t)}{7(t^2-1)^9}. \quad (\text{A9})$$

It contains the polynomial  $p^{(3)}(t)$  which reads as follows:

$$p^{(3)}(t) = 70 - 70t - 595t^2 + 595t^3 + 2280t^4 - 2280t^5 - 5309t^6 + 5309t^7 + 9134t^8 - 9134t^9 - 24077t^{10} - 49651t^{11} + 6532t^{12} + 20092t^{13} - 323t^{14} - 1725t^{15}. \quad (\text{A10})$$

Finally, the hexadecupole term reads as follows:

$$Q_4^{(\text{H})}(\omega) = \frac{t^2 p^{(4)}(t)}{9(1-t)^{11}(1+t)^{11}} - \frac{262144t^{15}(t^2-4)(t^2-9)(t^2-16)f(t)}{9(t^2-1)^{11}}. \quad (\text{A11})$$

The polynomial  $p^{(4)}(t)$  is given by

$$p^{(4)}(t) = 14175 - 14175t - 150255t^2 + 150255t^3 + 732060t^4 - 732060t^5 - 2191500t^6 + 2191500t^7 + 4624386t^8 - 4624386t^9 - 8049042t^{10} + 8049042t^{11} + 23686124t^{12} + 51811348t^{13} - 7367996t^{14} - 24613572t^{15} + 484375t^{16} + 3316713t^{17} + 14153t^{18} - 145225t^{19}. \quad (\text{A12})$$

The asymptotic limits are as follows. For high photon energy, one obtains the result

$$Q_\ell^{(\text{H})}(\omega) = \frac{2^{2\ell-1} \Gamma(2\ell+3)}{2\ell+1} \frac{1}{\omega} + \mathcal{O}\left(\frac{1}{\omega^2}\right). \quad (\text{A13})$$

By contrast, the result in the static limit is

$$Q_\ell^{(\text{H})}(\omega=0) = \frac{2(\ell+2)}{\ell(\ell+1)} \Gamma(2\ell+3), \quad (\text{A14})$$

for the general multipole order  $2^\ell$ . For the static value of the polarizability, one multiplies the result given in Eq. (A14) by a factor 2. The result (A14) can be used in Eqs. (30), (36), (42), and (48), in order to obtain long-range asymptotics for a perfect conductor. For positronium, one multiplies the result given in Eq. (A14) by  $2^{2\ell+1}$  in order to obtain the static limit of the  $2^\ell$ -pole polarizability of positronium.

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