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Long-range atom-wall interactions and mixing terms: Metastable hydrogen

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We investigate the interaction of metastable $2S$ hydrogen atoms with a perfectly conducting wall, including parity-breaking S-P mixing terms (with full account of retardation). The neighboring $2P_{1/2}$ and $2P_{3/2}$ levels are found to have a profound effect on the transition from the short-range, nonrelativistic regime, to the retarded form of the Casimir-Polder interaction. The corresponding P state admixtures to the metastable $2S$ state are calculated. We find the long-range asymptotics of the retarded Casimir-Polder potentials and mixing amplitudes for general excited states, including a fully quantum electrodynamic treatment of the dipole-quadrupole mixing term. The decay width of the metastable $2S$ state is roughly doubled even at a comparatively large distance of 918 a.u. (Bohr radii) from the perfect conductor. The magnitude of the calculated effects is compared to the unexplained Sokolov effect.

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Introduction.—The investigation of atom-wall interactions for atoms in contact with conducting materials has a long history. Starting from the works of Lennard-Jones [1], Bardeen [2], Casimir and Polder [3], and Lifshitz [4], research on related matters has found continuously growing interest over the last decades [5–8]. In the nonretarded regime (close range), the interaction energy scales as $1/\mathcal{Z}^3$ with the atom-wall distance $\mathcal{Z}$, while for atom-wall distances large in comparison to a typical atomic wavelength, the interaction energy scales as $1/\mathcal{Z}^4$ (see Chap. 8 of Ref. [9]). The leading term is given by virtual dipole transitions, while multipole corrections have recently been analyzed in Ref. [10]. The symmetry breaking induced by the wall leads to dipole-quadrupole mixing terms, which lead to admixtures to metastable levels [11,12]. While this effect has been analyzed in the nonretarded van der Waals regime [11,12], a fully quantum electrodynamic calculation of this effect would be of obvious interest.

This fact is emphasized by the curious observation of a long-range, and conceivably super-long-range (micrometer-scale) interaction of metastable hydrogen $2S$ atoms with a conducting surface (the so-called Sokolov effect, see Refs. [13–16]). It is not far-fetched to suspect that this effect could be due to a quantum electrodynamically induced tail of the dipole-quadrupole mixing term in the atom-wall interaction. Namely, for the hydrogen $2S$ atom, the neighboring $2P_{1/2}$ and $2P_{3/2}$ levels are removed only by the Lamb shift and fine structure, respectively, while it is known that virtual states of lower energy can induce long-range tails in atom-wall interactions, as well as in the Lamb shift between plates (see Refs. [17–26]). The large admixtures typically induced in atomic systems when a metastable level couples to nearly degenerate states of opposite parity suggest that a closer investigation of the hydrogen system is warranted. Atomic units with $\hbar = 4\pi\epsilon_0 = 1$ and $c = 1/\alpha$ are used throughout this Rapid Communication, where α is the fine-structure constant. The electron charge is explicitly denoted as e unless stated otherwise.

Retardation of the atom-wall interaction.—The quantum electrodynamic (QED) length-gauge interaction,

$$H_I = -e\,\vec{r}\cdot\vec{E} - \frac{e}{2} r^i\, r^j\, \partial E^i/\partial r^j + \cdots, \tag{1}$$

follows naturally from the formalism of a long-wavelength QED interaction Hamiltonian [27,28] ($\vec{r}$ denotes the electron coordinate). In contrast to the vector potential, the electric field strength (operator) is gauge-invariant (this point has given rise to some discussion, see Ref. [29]) and reads as [cf. Eq. (2.3) of Ref. [20]]

$$\begin{aligned}\vec{E}(\vec{r}) = \int_0^\infty dL \int_{\mathbb{R}^2} \frac{d^2k_\parallel}{\pi}\sqrt{\omega}\Bigg\{ & a_1(\vec{k},L)(\hat{k}_\parallel\times\hat{e}_z)\sin(Lz) \\ & + a_2(\vec{k},L)\left[\hat{k}_\parallel\,\frac{iL}{\omega}\sin(Lz) - \hat{e}_z\,\frac{k_\parallel}{\omega}\cos(Lz)\right]\Bigg\} \\ & \times\, e^{i\vec{k}_\parallel\cdot\vec{r}_\parallel} + \text{H.c.},\end{aligned} \tag{2}$$

where $\vec{r} = \vec{r}_\parallel + z\,\hat{e}_z$ with $\vec{r}_\parallel = x\,\hat{e}_x + y\,\hat{e}_y$, while $\vec{k}_\parallel = k_x\,\hat{e}_x + k_y\,\hat{e}_y$, also $\vec{k}_\perp = k_z\,\hat{e}_z$ and $L \equiv |\vec{k}_\perp|$. The commutator relation is $[a_s(\vec{k}_\parallel,L), a^\dagger_{s'}(\vec{k}_\parallel,L)] = \delta_{ss'}\,\delta^{(2)}(\vec{k}_\parallel - \vec{k}'_\parallel)\,\delta(L-L')$ for the annihilation and creation operators a_s and $a^\dagger_s$. In order to evaluate the interaction Hamiltonian (1), one shifts $z \to \mathcal{Z} + z$ where $\mathcal{Z}$ is the coordinate of the atom's center (nucleus). The proton is at $(0,0,\mathcal{Z})$, while the atomic electron coordinates are $(x,y,\mathcal{Z}+z)$. The surface of the perfect conductor is in the xy plane, i.e., in the plane described by the points $(x,y,0)$. The unperturbed Hamiltonian H_0 is the sum of the free radiation field and the unperturbed atom [see Eq. (2.1) of Ref. [20] and Eq. (3.2) of Ref. [30]]. For a reference ground state $|n\rangle$, second-order perturbation theory leads to a known result given in Eq. (8.41) of Ref. [9] or Eq. (27) of Ref. [10], which involves the symmetric sum with imaginary frequency in the argument of the dynamics polarizability $\Pi(\pm i\omega)$. The Wick rotation of the virtual photon integration contour leads to the symmetrization $i\omega \leftrightarrow -i\omega$ but cannot be done for excited reference states. We use second-order perturbation theory to evaluate $\Delta E = \langle n|(-e\,\vec{r}\cdot\vec{E})\,[1/(E_n - H_0')]\,(-e\,\vec{r}\cdot\vec{E})|n\rangle$ and

obtain [cf. the discussion following Eq. (2.12) of Ref. [20]]

$$\Delta E \doteq \frac{e^2}{2\pi}\,\mathrm{P}\sum_q \int_0^\infty dL \int_L^\infty d\omega\,\cos(2L\,\mathcal{Z})\,\frac{L^2\,(|\langle n|\vec{r}_\parallel|q\rangle|^2+2|\langle n|z|q\rangle|^2)+\omega^2(|\langle n|\vec{r}_\parallel|q\rangle|^2-2|\langle n|z|q\rangle|^2)}{\mathcal{E}_q+\omega-i\,\delta}, \tag{3}$$

where P denotes the principal value. Here, the identity $\int_{\mathbb{R}^3} d^3k = 2\int_0^{2\pi} d\varphi \int_0^\infty dL \int_0^\infty d\omega\,\omega$, with $\omega = \sqrt{\vec{k}_\parallel^2 + k_z^2}$, and $L = |k_z|$ has been used in order to transform the integration measure. The virtual states are denoted as $|q\rangle$, and their energy difference to the reference state is denoted as $\mathcal{E}_q \equiv E_q - E_n$. In contrast to the velocity gauge [20], there is no seagull term to consider, and it is not necessary to add the electrostatic interaction with the mirror charges by hand [31]. It is an in principle well-known (see the remarks following Eq. (A.22) in Appendix A of Ref. [32]), but sometimes forgotten, wisdom that the Coulomb interaction does not need to be quantized in the velocity gauge [31]. The integration with respect to ω leads to logarithmic terms [see the Appendix of Ref. [20]]. After the subtraction of $\mathcal{Z}$-independent terms (the subtraction is denoted by the $\doteq$ sign), one obtains

$$I_1(\chi) \doteq \int_0^\infty dL\,\cos(2L\mathcal{Z})\,\ln(|\mathcal{E}_q+L|) = \mathcal{E}_q\left(\frac{\pi\,[1-\varepsilon(\mathcal{E}_q)]}{2\chi} - \frac{T(\chi)}{\chi} - \pi\,\Theta(-\mathcal{E}_q)\,\frac{2\sin^2\left(\frac{\chi}{2}\right)}{\chi}\right), \tag{4a}$$

$$I_2(\chi) \doteq -\frac{\partial^2 I_1}{\partial\chi^2} = \mathcal{E}_q\left(\frac{\pi\,[\varepsilon(\mathcal{E}_q)-1]+\chi}{\chi^3} + \frac{2-\chi^2}{\chi^3}\,T(\chi) - \frac{2}{\chi^2}\,U(\chi) + \pi\,\Theta(-\mathcal{E}_q)\,\frac{\partial^2}{\partial\chi^2}\,\frac{2\sin^2\left(\frac{\chi}{2}\right)}{\chi}\right), \tag{4b}$$

$$T(\chi) = \sin(\chi)\,\mathrm{Ci}(\chi) - \cos(\chi)\,\mathrm{Si}(\chi) + \frac{\pi}{2}\cos(\chi), \quad \chi = 2|\mathcal{E}_q|\,\mathcal{Z}, \quad \varepsilon(\mathcal{E}_q) = \Theta(\mathcal{E}_q) - \Theta(-\mathcal{E}_q). \tag{4c}$$

Here, $\mathrm{Ci}(\chi) = -\int_\chi^\infty dt\,\frac{\cos(t)}{t}$ and $\mathrm{Si}(\chi) = \int_0^\chi dt\,\frac{\sin(t)}{t}$, and $U(\chi) = \frac{\partial}{\partial\chi}T(\chi)$, while $T(\chi) = \chi^{-1} - \frac{\partial}{\partial\chi}U(\chi)$. We confirm the result given in Eq. (2.18) of Ref. [20] and represent the "distance-dependent Lamb shift" as

$$\begin{aligned}\Delta E \doteq \frac{e^2}{2\pi}\sum_q \mathcal{E}_q^3 \Bigg\{&(|\langle n|\vec{r}_\parallel|q\rangle|^2 - 2|\langle n|z|q\rangle|^2)\left[\frac{\pi\,[\varepsilon(\mathcal{E}_q)-1]}{2\chi} - \frac{1}{\chi^2} + \frac{T(\chi)}{\chi} + \pi\,\Theta(-\mathcal{E}_q)\,\frac{1-\cos(\chi)}{\chi}\right]\\ &- (|\langle n|\vec{r}_\parallel|q\rangle|^2 + 2|\langle n|z|q\rangle|^2)\left[\frac{\pi\,[\varepsilon(\mathcal{E}_q)-1]+\chi}{\chi^3} + \frac{2-\chi^2}{\chi^3}\,T(\chi) - \frac{2}{\chi^2}\,U(\chi) + \pi\,\Theta(-\mathcal{E}_q)\,\frac{\partial^2}{\partial\chi^2}\,\frac{1-\cos(\chi)}{\chi}\right]\Bigg\}.\end{aligned} \tag{5}$$

We should perhaps clarify that the $\mathcal{Z}$-independent contribution to the Lamb shift (the ordinary "free-space Lamb shift") is absorbed in the subtraction procedure denoted here by the "$\doteq$" sign in Eqs. (4), (5), (7), and (8). The $\mathcal{Z}$-dependent position of the energy level is obtained after adding the free-space Lamb shift $\mathcal{L}$ and free-space fine structure $\mathcal{F}$ given in Eq. (12) to the $\mathcal{Z}$-dependent energy shifts given in Eqs. (5) and (8). In the nonretardation limit, the $\mathcal{Z}$-dependent results given in Eqs. (5) and (8) are replaced by the respective terms of the nonretarded potential (11). This (somewhat subtle) point is not fully discussed in previous works on the subject [17–21] and therefore should be mentioned for absolute clarity.

The term $-\chi^{-2}$ in the coefficient multiplying $|\langle n|\vec{r}_\parallel|q\rangle|^2 - 2\,|\langle n|\vec{z}|q\rangle|^2$ vanishes after summing over the entire spectrum of virtual states; it is obtained naturally in the length gauge and otherwise cancels a term in the expansion of the energy shift for large χ (even before the application of the sum rule, which is crucial in velocity gauge [20]). The off-diagonal mixing term leads to the matrix element $\Delta M = \langle m|(-e\,\vec{r}\cdot\vec{E})\,[1/(E_n - H_0)'](-\frac{e}{2}r^i\,r^j\,(\partial E^i/\partial r^j))|n\rangle + \langle m|\mathrm{H.c.}|n\rangle$,

$$\Delta M = \frac{e^2}{4\pi}\mathrm{P}\sum_q \int_0^\infty dL \int_L^\infty d\omega\,\frac{L\,\sin(2\,L\,\mathcal{Z})}{\mathcal{E}_q+\omega-i\delta}\,(L^2\,\langle n|\mathcal{T}_2|m\rangle - \omega^2\,\langle n|\mathcal{T}_1|m\rangle), \tag{6a}$$

$$\langle m|\mathcal{T}_1|n\rangle = \langle m|z|q\rangle\,\langle q|\vec{r}_\parallel^{\,2} - 2\,z^2|n\rangle + \langle m|\mathrm{H.c.}|n\rangle, \tag{6b}$$

$$\langle m|\mathcal{T}_2|n\rangle = \langle m|z|q\rangle\,\langle q|\vec{r}_\parallel^{\,2} - 2\,z^2|n\rangle - 2\,\langle m|\vec{r}_\parallel|q\rangle\cdot\langle q|\vec{r}_\parallel\,z|n\rangle + \langle m|\mathrm{H.c.}|n\rangle. \tag{6c}$$

After the subtraction of $\mathcal{Z}$-independent terms, the following two results for $J_1(\chi) = \int_0^\infty dL\;\; L\sin(2L\mathcal{Z})\ln(|\mathcal{E}_q+L|)$ and $J_2(\chi) = -\partial^2 J_1(\chi)/\partial\chi^2$ supplement the analytic integrals given in Eq. (4),

$$J_1(\chi) \doteq \mathcal{E}_q^2\left(\varepsilon(\mathcal{E}_q)\left[\frac{\pi}{2\chi^2} - \frac{T(\chi)}{\chi^2} + \frac{U(\chi)}{\chi}\right] - \frac{\pi}{2\chi^2} + \pi\,\Theta(-\mathcal{E}_q)\,\frac{2\sin^2\left(\frac{\chi}{2}\right) - \chi\sin(\chi)}{\chi^2}\right), \tag{7a}$$

$$J_2(\chi) \doteq \mathcal{E}_q^2\left(\frac{3\,\pi}{\chi^4} + \varepsilon(\mathcal{E}_q)\left[\frac{4\chi-3\pi}{\chi^4} + \frac{3\,(2-\chi^2)}{\chi^4}\,T(\chi) + \frac{\chi^2-6}{\chi^3}\,U(\chi)\right] - \pi\,\Theta(-\mathcal{E}_q)\,\frac{\partial^2}{\partial\chi^2}\,\frac{2\sin^2\left(\frac{\chi}{2}\right) - \chi\sin(\chi)}{\chi^2}\right). \tag{7b}$$

We can finally give the complete result for the mixing term ΔM, with full account of retardation, as a sum over virtual states $|q\rangle$,

$$\Delta M \doteq \frac{e^2}{4\pi}\sum_q \mathcal{E}_q^4 \left\{ \langle m|\mathcal{T}_1|n\rangle \left[\varepsilon(\mathcal{E}_q)\left(\frac{4+\pi\chi}{2\chi^3} - \frac{T(\chi)}{\chi^2} + \frac{U(\chi)}{\chi}\right) - \frac{\pi}{2\chi^2} + \pi\Theta(-\mathcal{E}_q)\,\frac{2\sin^2\left(\frac{\chi}{2}\right) - \chi\,\sin(\chi)}{\chi^2}\right] \right.$$
$$\left. + \langle m|\mathcal{T}_2|n\rangle \left[\varepsilon(\mathcal{E}_q)\left(\frac{3\pi-4\chi}{\chi^4} + \frac{3(\chi^2-2)}{\chi^4}T(\chi) + \frac{6-\chi^2}{\chi^3}U(\chi)\right) - \frac{3\pi}{\chi^4} + \pi\Theta(-\mathcal{E}_q)\frac{\partial^2}{\partial\chi^2}\,\frac{2\sin^2\left(\frac{\chi}{2}\right) - \chi\,\sin(\chi)}{\chi^2}\right]\right\}. \tag{8}$$

The energy variable $\mathcal{E}_q$ is defined with respect to the reference state; i.e., if one evaluates the $|m\rangle$-state admixture to the reference state $|n\rangle$, then one sets $\mathcal{E}_q = E_q - E_n$. For excited reference states, results for both ΔE given in Eq. (5) and ΔM in Eq. (8) contain long-range retardation tails for excited reference states,

$$\Delta E = e^2\sum_q \Theta(-\mathcal{E}_q)\left[|\langle n|\vec{r}_\parallel|q\rangle|^2\left(\frac{\mathcal{E}_q^2\,\cos(2\mathcal{E}_q\mathcal{Z})}{2\mathcal{Z}} - \frac{\mathcal{E}_q\,\sin(2\mathcal{E}_q\mathcal{Z})}{4\mathcal{Z}^2} - \frac{\cos(2\mathcal{E}_q\mathcal{Z})}{8\mathcal{Z}^3}\right)\right.$$
$$\left. - |\langle n|z|q\rangle|^2\left(\frac{\mathcal{E}_q\,\sin(2\,\mathcal{E}_q\,\mathcal{Z})}{\mathcal{Z}^2} + \frac{\cos(2\mathcal{E}_q\mathcal{Z})}{4\,\mathcal{Z}^3}\right)\right] - \frac{1}{8\,\pi\,\mathcal{Z}^4}\,(2\Pi_\parallel + \Pi_\perp), \quad \mathcal{Z} \gg \frac{1}{\mathcal{E}_q},$$
$$\Pi_\parallel = \frac{1}{2}\sum_{q,\pm}\frac{2}{\mathcal{E}_q}\,\langle n|\vec{r}_\parallel|q\rangle\cdot\langle q|\vec{r}_\parallel|n\rangle, \quad \Pi_\perp = \sum_{q,\pm}\frac{2}{\mathcal{E}_q}|\langle n|z|q\rangle|^2, \quad \Pi(\omega) = \frac{e^2}{3}\sum_\pm \langle n|r^i\left(\frac{1}{\mathcal{E}_q \pm \omega}\right)r^i|n\rangle, \tag{9}$$

where $\Pi_\parallel$ and $\Pi_\perp$ are the longitudinal and transverse static polarizabilities [for the ground state, $\Pi_\perp = \Pi_\parallel = \Pi(0)$]. The mixing term has the following long-range asymptotics:

$$\Delta M = e^2\sum_q \Theta(-\mathcal{E}_q)\,\langle m|\vec{r}_\parallel|q\rangle\cdot\langle q|\vec{r}_\parallel\,z|n\rangle\left(-\frac{\mathcal{E}_q^3\sin(2\mathcal{E}_q\,\mathcal{Z})}{4\mathcal{Z}} - \frac{3\,\mathcal{E}_q^2\cos(2\mathcal{E}_q\,\mathcal{Z})}{8\mathcal{Z}^2} + \frac{3\,\mathcal{E}_q\,\sin(2\mathcal{E}_q\,\mathcal{Z})}{8\mathcal{Z}^3} + \frac{3\,\mathcal{E}_q^4\,\cos(2\mathcal{E}_q\,\mathcal{Z})}{16\mathcal{Z}^4}\right)$$
$$+ e^2\sum_q \Theta(-\mathcal{E}_q)\,\langle m|z|q\rangle\langle q|\vec{r}_\parallel^{\,2} - 2z^2|n\rangle\left(\frac{\mathcal{E}_q^2\,\cos(2\mathcal{E}_q\,\mathcal{Z})}{8\mathcal{Z}^2} - \frac{3\,\mathcal{E}_q\,\sin(2\mathcal{E}_q\,\mathcal{Z})}{16\mathcal{Z}^3} - \frac{3\,\cos(2\mathcal{E}_q\,\mathcal{Z})}{32\mathcal{Z}^4}\right)$$
$$+ \frac{e^2}{\pi\,\mathcal{Z}^5}\sum_q\frac{1}{\mathcal{E}_q}\left(-\frac{1}{8}\,\langle m|z|q\rangle\,\langle q|\vec{r}_\parallel^{\,2}|n\rangle + \frac{1}{4}\,\langle m|z|q\rangle\,\langle q|z^2|n\rangle + \frac{3}{8}\,\langle m|\vec{r}_\parallel|q\rangle\cdot\langle q|\vec{r}_\parallel\,z|n\rangle\right) + \langle m|\mathrm{H.c.}|n\rangle, \quad \mathcal{Z} \gg \frac{1}{\mathcal{E}_q}. \tag{10}$$

The results (5) and (8) will now be applied to metastable hydrogen.

Nonretarded admixtures to metastable hydrogen.—The results given in Eqs. (5) and (8) have a rather involved analytic structure. In the short-range limit, these results can be compared to the static interaction of the electron and proton [33,34] with their respective mirror charges. This interaction leads to the following nonretarded potential (from now on we set the elementary charge $e = 1$),

$$V = \frac{1}{2}\left(-\frac{1}{2(z+\mathcal{Z})} + \frac{2}{\sqrt{x^2+y^2+(z+2\mathcal{Z})^2}} - \frac{1}{2\mathcal{Z}}\right)$$
$$= -\frac{\vec{r}_\parallel^{\,2}+2z^2}{16\,\mathcal{Z}^3} + \frac{3z(\vec{r}_\parallel^{\,2}+2z^2)}{32\,\mathcal{Z}^4} + \cdots, \tag{11}$$

where we ignore terms of order $1/\mathcal{Z}^5$ and higher [35,36]. After some tedious, but straightforward algebra, one can convince oneself that the terms of order $\mathcal{Z}^{-3}$ and $\mathcal{Z}^{-4}$ are in agreement with the short-range asymptotics of the results given in Eqs. (5) and (8), i.e., in the regime $\mathcal{Z} \ll 1/\mathcal{E}_q$, which is equivalent to the limit $\chi \to 0$.

For close approach of the atom to the wall, the interaction energy is well described by the static potential (11), which necessitates a diagonalization of the Schrödinger Hamiltonian plus the nonretarded potential V (both "diagonal" interaction and Lamb-shift or fine-structure terms, as well as "mixing" terms) in the basis of the $|2S_{1/2}\rangle$,$|2P_{1/2}\rangle$, and $|2P_{3/2}\rangle$ Schrödinger-Pauli wave functions with magnetic projection $\mu = +1/2$, to form the manifestly coupled states $|\mathcal{S}_{1/2}\rangle$,$|\mathcal{P}_{1/2}\rangle$, and $|\mathcal{P}_{3/2}\rangle$. We denote the (free-space) fine-structure and the Lamb-shift interval as

$$\mathcal{F} = 1.66\times10^{-6}\,\mathrm{a.u.}, \quad \mathcal{L} = 1.61\times10^{-7}\,\mathrm{a.u.}, \tag{12}$$

respectively. According to the adiabatic theorem [37–39], the $|\mathcal{S}_{1/2}\rangle$ state eigenvector has the form

$$|\mathcal{S}_{1/2}\rangle \approx a_S\,|2S_{1/2}\rangle + a_{\frac{1}{2}}\,|2P_{1/2}\rangle + a_{\frac{3}{2}}\,|2P_{3/2}\rangle, \tag{13a}$$

$$a_S = 1, \quad a_{\frac{1}{2}} = \frac{\sqrt{3}}{2}\,\frac{15}{\mathcal{L}\,\mathcal{Z}^4}, \quad a_{\frac{3}{2}} = \sqrt{\frac{3}{2}}\,\frac{15}{\mathcal{F}\,\mathcal{Z}^4}, \tag{13b}$$

$$1/\mathcal{L} \gg \mathcal{Z} \gg 1/\mathcal{L}^{1/4}, \quad 1/\mathcal{Z} \gg \mathcal{Z} \gg 1/\mathcal{F}^{1/4}, \tag{13c}$$

where we ignore higher-order terms in the expansion in inverse powers of $\mathcal{Z}$. The absolute square of the admixture is given by

$$\Xi = \frac{675}{2}\left(\frac{1}{\mathcal{F}^2} + \frac{1}{2\,\mathcal{L}^2}\right)\frac{1}{\mathcal{Z}^8} = \frac{6.63\times10^{15}}{\mathcal{Z}^8}\,\mathrm{a.u.} \tag{14}$$

The one-photon decay width of the $2P$ state is given as $\Gamma_{2P} = 6.27 \times 10^8 \, \frac{\text{rad}}{\text{s}} = 1.51 \times 10^{-8}$ a.u., whereas the two-photon decay width of the $2S$ state reads $\Gamma_{2S} = 8.229 \, \frac{\text{rad}}{\text{s}} = 1.99 \times 10^{-16}$ a.u. The effective decay rate Γ_{eff} at a distance $\mathcal{Z}$ is

$$\Gamma_{\text{eff}} = \Gamma_{2S} + \Gamma_{2P}\,\Xi = \left(1.99 \times 10^{-16} + \frac{1.01 \times 10^8}{\mathcal{Z}^8}\right) \text{a.u.} \tag{15}$$

We have $\Gamma_{\text{eff}} = 2\,\Gamma_{2S}$ for $\mathcal{Z}_0 = 918$ a.u. The leading (non-retarded) term in the atom-wall energy shift at this distance amounts to $-7\mathcal{Z}_0^{-3}/2 = -4.52 \times 10^{-9}$ a.u. and approximates both the single-particle perturbative shift given in Eq. (5) as well as the adiabatic energy of the coupled $|\mathcal{S}_{1/2}\rangle$ state obtained from the diagonalization of the potential (11) to within 10%. The atom-wall energy at $\mathcal{Z}_0$ is equal to -29.7 MHz and thus much smaller than the Lamb shift and fine structure.

The admixture formulas for the coupled $|\mathcal{P}_{1/2}\rangle$ state reads as

$$|\mathcal{P}_{1/2}\rangle \approx b_S\,|2S_{1/2}\rangle + b_{1/2}\,|2P_{1/2}\rangle + b_{3/2}\,|2P_{3/2}\rangle, \tag{16a}$$

$$b_S = -\sqrt{\frac{3}{4}}\,\frac{15}{\mathcal{L}\,\mathcal{Z}^4}, \quad b_{\frac{3}{2}} = \frac{1}{2\sqrt{2}}\,\frac{1}{\mathcal{F}\,\mathcal{Z}^3}, \tag{16b}$$

and $b_{\frac{1}{2}} = 1$. The $|\mathcal{P}_{3/2}\rangle$ state reads as

$$|\mathcal{P}_{3/2}\rangle \approx c_S\,|2S_{1/2}\rangle + c_{1/2}\,|2P_{1/2}\rangle + c_{3/2}\,|2P_{3/2}\rangle, \tag{17a}$$

$$c_S = -\sqrt{\frac{3}{2}}\,\frac{15}{\mathcal{F}\,\mathcal{Z}^4}, \quad c_{\frac{1}{2}} = \frac{1}{2\sqrt{2}}\,\frac{1}{(\mathcal{L}+\mathcal{F})\,\mathcal{Z}^3}, \tag{17b}$$

and of course $c_{\frac{3}{2}} = 1$. For very close approach $Z \lesssim 300$, higher-order terms in the expansion of the potential V [see Eq. (11)] gradually become important. [These are obtained by straightforward expansion of the potential (11).] Numerically determined admixtures of the coupled $|\mathcal{S}_{1/2}\rangle$ are given in Fig. 1, they do not follow the asymptotic formulas for very close approach.

Long-range tails.—The oscillatory repulsive-attractive dominant term in the long-range limit of the energy shift for the $2S$ level goes as [see Eqs. (5) and (9)]

$$\Delta E_{2S} \sim \frac{9\mathcal{L}^2\,\cos(2\mathcal{L}\,\mathcal{Z})}{2\mathcal{Z}}, \quad \mathcal{Z} \gg \frac{1}{\mathcal{L}}, \tag{18}$$

where we have isolated the leading term from Eq. (9), setting $\mathcal{E}_q = -\mathcal{L}$ and carrying the summation over the virtual levels $|q\rangle = |2P_{1/2}\rangle$ with magnetic projections $\mu = \pm 1/2$. Somewhat surprisingly, the oscillatory terms in Eq. (10) vanish for virtual $|2P_{1/2}\rangle$ states, so that the long-range coupling to the lower-lying P state vanishes. The leading terms in the long-range asymptotics of the admixture coefficients read as [see Eq. (13)]

$$a_{1/2} \sim \frac{3\sqrt{3}}{\pi\,\mathcal{L}\,\mathcal{F}\,\mathcal{Z}^5}, \quad \mathcal{Z} \gg \frac{1}{\mathcal{L}}, \tag{19a}$$

$$a_{3/2} \sim -\sqrt{\frac{3}{2}}\,\frac{3\mathcal{L}^3}{\mathcal{F}\,\mathcal{Z}}\,\sin(2\mathcal{L}\,\mathcal{Z}), \quad \mathcal{Z} \gg \frac{1}{\mathcal{L}}. \tag{19b}$$

The long-range asymptotic tail of the $P_{3/2}$-state admixture has an oscillatory $(1/\mathcal{Z})$ form [see Eqs. (10) and (19b)]. If this tail had not been suppressed by the prefactor $\mathcal{L}^3/\mathcal{F}$, then it could have easily provided a theoretical explanation for the Sokolov effect [13–16], because the $(1/\mathcal{Z})$ interaction has the required functional form to describe a super-long-range term. The tail is created by virtual $|q\rangle = |2P_{1/2}\rangle$ states in Eq. (10), which are energetically lower than the reference $|2S\rangle$ state. The prefactor of the super-long-range tail of the admixture term depends on details of the spectrum of the atomic system and could be larger for other atoms. For the $P_{1/2}$-state admixture (term $a_{1/2}$), retardation changes the $1/\mathcal{Z}^4$ asymptotics for short range to a $1/\mathcal{Z}^5$ asymptotics at long range. A full QED treatment of the admixture terms is required for both results recorded in Eqs. (19a) and (19b).

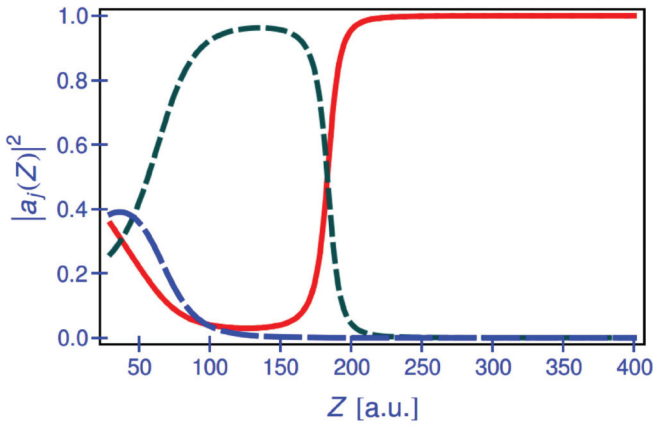

FIG. 1. (Color) The modulus-squared admixtures to the coupled $|\mathcal{S}_{1/2}\rangle$ state are obtained from a diagonalization of the potential (11) in the basis of $|\mathcal{S}_{1/2}\rangle$,$|\mathcal{P}_{1/2}\rangle$, and $|\mathcal{P}_{3/2}\rangle$ states, for close approach of the atom toward the wall. The subscript j in Eq. (13) takes on the values $j = S$, as well as $j = 1/2$ and $j = 3/2$, and denotes the state responsible for the admixture. As the $|\mathcal{S}_{1/2}\rangle$ state approaches the wall, the initially dominant $|S_{1/2}\rangle$ state contribution (solid curve, $j = S$) gradually fades and the $|P_{1/2}\rangle$ admixture (short-dashed curve, $j = 1/2$) increases, while a significant admixture of the $|P_{3/2}\rangle$ state (long-dashed curve, $j = 3/2$) is observed only for close approach. The atom-wall interaction energy becomes commensurate with the Lamb shift and fine structure at $\mathcal{Z} \approx 84$ and $\mathcal{Z} \approx 184$, respectively.

Conclusions.—We can safely conclude that the curious observations reported in [13–16] regarding super-long-range $2S$-$2P$ mixing terms near metal surfaces cannot find an explanation in terms of a long-range effect involving quantum fluctuations. Both the energy shift (9) as well as the mixing term (10) have long-range tails proportional to $1/\mathcal{Z}$, but the energy numerator for the $2S$-$2P_{1/2}$ transition is so small (Lamb shift, a 30-cm wavelength transition) that the region in which the $1/\mathcal{Z}$ terms dominate is restricted to excessively large atom-wall separations where the single power of $\mathcal{Z}$ in the denominator is sufficient to make the interaction energy and admixture terms negligible. (We should add that the inclusion of additional mirror charges in a cavity as opposed to a wall can be taken into account, in the short-range limit, by summing the mirror charge interactions into a generalized Riemann ζ function [40] and therefore cannot change the order of magnitude of the admixture terms.)

If the observations reported in Refs. [13–16] had found a natural explanation in terms of a QED effect, then this might

have had significant implications for a typical atomic beam apparatus [41] used in high-precision spectroscopy of atoms, potentially shifting the frequency of transitions involving $2S$ atoms in a narrow tube. For atom-wall separations smaller than 1000 Bohr radii, substantial admixture terms are found, and the $1/\mathcal{Z}^8$ scaling of the effective $2S$ decay rate predicted by Eq. (14) could be tested against an experiment. The clarification of the parity-breaking admixture terms also is important for other precision measurements in atomic physics which involve metastable states, such as electron dipole moment (EDM) and weak-interaction experiments [42–47]. The fully retarded expression for the mixing term, given in Eq. (10), formulates higher-order QED corrections to atom-wall interactions beyond dipole order. Generalization of the formulas to, e.g., the 2^3S_1 metastable state of helium is straightforward. One just sums the interactions over the electron coordinates.

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