Longitudinal fields in interactions between atoms and absorptive dielectrics

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The properties of atoms close to an absorptive dielectric are studied using the phenomenological Maxwell's equations. Although radiative decay has been considered by many authors, the coupling of atoms with longitudinal modes does not seem to have been treated in detail. Here we show that there are two main effects. The first is a change in the atomic interaction potential from the Coulomb one to a static potential, i.e., one that satisfies a Poisson equation featuring the static dielectric function $\varepsilon_{\text{stat}} = \varepsilon(\omega)|_{\omega=0}$. The second is the decay of excited atomic states through longitudinal field interactions. We find that the corresponding decay constant is nonzero only for atom-dielectric distances in the order of an atomic diameter and that it decreases exponentially fast on an atomic scale with increasing distance. We also show that the Hamiltonian used by the Jena group [Dung *et al.*, Phys. Rev. A **65**, 043813 (2002)], featuring the Coulomb potential, is unitarily equivalent to one containing the static potential.

I. INTRODUCTION

A. Background

From a microscopic point of view the interactions in a system of nonrelativistic charged particles and the quantized vacuum electromagnetic field in the Coulomb gauge can be described in terms of the Coulomb potentials between the particles and a minimal coupling interaction between charges and field. In practice, in view of the many degrees of freedom, processes such as the decay of an excited atom in the presence of a dielectric (for instance, a photonic crystal) are hard, if not impossible, to treat in this way. Instead a quantized version of the macroscopic (phenomenological) Maxwell's equations is often used to deal with such situations. An advantage of this approach is that the properties of the dielectric are now stored in a single object, the permittivity (electric permeability, dielectric function) $\varepsilon(\mathbf{x}, \omega)$, which is in general a complex function of position $\mathbf{x}$ and frequency ω. On the other hand, we have to remember that the macroscopic Maxwell's equations have a limited range of validity. The important thing here is that they can become unreliable on the scale of atomic dimensions. Also ionization phenomena are not incorporated and the atoms or ions constituting the dielectric remain in bound states. However, the latter can become perturbed, giving rise to polarization.

Another point is the interaction with the material of an atom embedded in the material or close to its boundary. One expects that the interaction of an embedded atom with its nearest neighbors is not correctly described. In a microscopic approach the interaction with radiative field modes involves the vector potential but now the microscopic and macroscopic vector potentials are in general different. The latter problem is often taken care of in an approximate way by using the so-called real cavity model, see Sec. IV.

A general issue, common to almost all problems where the deexcitation of an unstable state is considered, is the choice of the initial state. In the present case it is the decay of an excited embedded atom due to radiative or other processes. It is customary to describe the decay of such an unstable state as a time evolution problem starting at some finite initial time, say $t=0$. But then the question arises as to how this state is prepared. In the present situation, where matter-field interactions are involved, the initial state depends in addition on the employed gauge. From a more fundamental point of view the actual process is often a scattering process, where initially, at large negative times, a photon wave packet is prepared outside the medium and the resulting radiation is observed outside the medium at large positive times. This process is well-defined and less sensitive to gauge changes, see Ref. [1], Sec. X.

Returning to the case at hand the question is how to excite the atom selectively, for instance, through photon absorption. Obviously, if the atomic transition frequency ω_0 is in the order of some internal transition frequency ω_i of the material this is only possible if the atom is well separated from the dielectric, which is an uninteresting case. However, if an ω_i is present with $\omega_0 \approx \omega_i$ the material would be very strongly absorbing, i.e., not a dielectric at all. Here we note that, due to the interaction with the material the atomic levels will be shifted and possibly broadened if some absorption takes place. This happens to a lesser extend for the often used rare earth atoms, where the active electron is an inner shell one that is somewhat screened from its surroundings.

Thus, if the atomic transition frequencies differ appreciably from those in the material, selective excitation becomes possible. This is the situation we consider in the present work. In practice the situation can be more complex. Rare earth atoms, for instance, are difficult to excite directly. Here a so-called sensitizer (a large molecule), close to the atom, is excited initially. Its excitation energy is then converted to the atom, leaving it in a higher excited state. Subsequently it loses part of its energy to its surroundings and the atom ends up in the excited state of interest.

In the sequel we discuss, from the macroscopic point of view, some aspects of longitudinal interactions of atoms (ions, molecules) with absorptive dielectrics. So far the emphasis has usually been on transverse interactions with the fields since these are responsible for radiative decay processes. However, longitudinal interactions are also present and here we investigate the latter somewhat further.

As mentioned above, in the vacuum case, using the Coulomb gauge, the longitudinal atom-field interactions result in Coulomb potentials between the charges constituting the atom, whereas the coupling with the vacuum electromagnetic field involves the vector potential, which is transverse. All this changes if an absorptive dielectric is present. Then, in addition to transverse ones, there are also nonstatic longitudinal fields, which can be quantized along with the transverse fields. One can continue to use a transverse vector potential but then, in addition to the Coulomb potential, a second potential appears, which depends on the longitudinal field operators. This approach was taken by Dung *et al.* [2,3], who considered spontaneous atomic decay and intermolecular energy transfer. However, it is also possible to proceed differently. Then the Coulomb potential is modified but still does not contain field operators, whereas the vector potential inside the dielectric is no longer transverse. In fact both representations are related by a unitary transformation, as we show below in Sec. III.

The formalism we use here provides an interesting division into effects due to a modification of the Coulomb potential and effects related to the interaction of an atom with the quantized longitudinal field modes. For an atom in vacuum close to an interface with the absorptive dielectric, the first gives a correction proportional to an inverse power of the atom-dielectric distance, whereas the second shows an exponential decay on an atomic scale, i.e., with a half width in the order of an atomic diameter. Here we note that this involves a length scale on which the macroscopic equations become questionable. However, although numerically the result may be far off, its form is consistent with what one would expect from microscopic considerations.

Below we denote $(f,g) = \langle g | f \rangle$ and $\mathbf{e_a} = \mathbf{a}/|\mathbf{a}| = \mathbf{a}/a$. In the sequel we make use of the decomposition into longitudinal and transverse components of three-dimensional vector fields. This is usually done by writing the field as a sum of a divergence and a rotation

$$\mathbf{f}(\mathbf{x}) = \partial_{\mathbf{x}}\Phi(\mathbf{x}) + \partial_{\mathbf{x}} \times A(\mathbf{x}), \quad (1.1)$$

but this becomes a bit problematic in case $\mathbf{f}(\mathbf{x})$ has discontinuities. Therefore it is more convenient to give a definition through its Fourier transform $\tilde{\mathbf{f}}(\mathbf{k})$, which exists for any square integrable $\mathbf{f}(\mathbf{x})$. Then the longitudinal component is the part of $\tilde{\mathbf{f}}(\mathbf{k})$ along $\mathbf{k}$ and we define (U is the 3×3 unit matrix)

$$(\mathsf{P}^{\parallel} \cdot \tilde{\mathbf{f}})(\mathbf{k}) = \tilde{\mathbf{f}}^{\parallel}(\mathbf{k}) = \mathbf{e_k}\mathbf{e_k} \cdot \tilde{\mathbf{f}}(\mathbf{k}),$$

$$(\mathsf{P}^{\perp} \cdot \tilde{\mathbf{f}})(\mathbf{k}) = \tilde{\mathbf{f}}^{\perp}(\mathbf{k}) = (\mathsf{U} - \mathbf{e_k}\mathbf{e_k}) \cdot \tilde{\mathbf{f}}(\mathbf{k}), \quad (1.2)$$

which leads to the corresponding decomposition for any square integrable $\mathbf{f}(\mathbf{x})$.

B. An example from electrostatics

To set the stage we start with an example from electrostatics. Consider a fixed charge e, placed above a dielectric filling the half space $x_3 < 0$ with permittivity [$\theta(x)$ is the Heaviside step function]

$$\varepsilon(\mathbf{x}) = 1 + \chi\theta(-x_3). \quad (1.3)$$

The field in the half space $x_3 > 0$ is then given by [4]

$$E(\mathbf{x}) = -\partial_{\mathbf{x}}\left\{ \frac{e}{4\pi|\mathbf{x} - \mathbf{X}|} - \frac{\chi}{2 + \chi}\frac{e}{4\pi|\mathbf{x} + \mathbf{X}|} \right\}, \quad (1.4)$$

where $\mathbf{X} = X\mathbf{e}_3$, $\mathbf{e}_3 = (0,0,1)$, is the position of the charge. Thus an electron (charge $-e$, position $\mathbf{x}$) in $\mathbf{x}$ feels the above field and if the charge in $\mathbf{X}$ is a proton, so we are talking about a hydrogen atom, the electron moves in the potential

$$V = -\frac{e^2}{4\pi|\mathbf{x} - \mathbf{X}|} + \frac{\chi}{2 + \chi}\frac{e^2}{4\pi|\mathbf{x} + \mathbf{X}|} - \frac{\chi}{2 + \chi}\frac{e^2}{8\pi|x_3|}. \quad (1.5)$$

The last term expresses the electrostatic interaction of the electron, which is not supposed to be fixed, with the dielectric, in this case a mirror charge in $(x_1, x_2, -x_3)$.

In general, for a set of charged particles with positions $\mathbf{x}_n$, masses m_n, and charges e_n we have for the displacement D

$$D(\mathbf{x}) = \varepsilon(\mathbf{x})E(\mathbf{x}), \quad \partial_{\mathbf{x}} \cdot D(\mathbf{x}) = \rho(\mathbf{x}) = \sum_n e_n\delta(\mathbf{x} - \mathbf{x}_n) \quad (1.6)$$

and

$$E(\mathbf{x}) = -\partial_{\mathbf{x}}\Phi(\mathbf{x}), \quad \Phi(\mathbf{x}) = \sum_n e_n\varphi(\mathbf{x},\mathbf{x}_n),$$

$$-\partial_{\mathbf{x}} \cdot \varepsilon(\mathbf{x})\partial_{\mathbf{x}}\varphi(\mathbf{x},\mathbf{x}_n) = e_n\delta(\mathbf{x} - \mathbf{x}_n). \quad (1.7)$$

For charges above a dielectric half space, as above, the total potential is

$$V = \frac{1}{2}\sum_{m,n} e_m e_n\varphi(\mathbf{x}_m,\mathbf{x}_n), \quad (1.8)$$

where infinite self-interactions are deleted in the above sum, but interactions between a charge and the dielectric, such as the last contribution to V in Eq. (1.3), are retained.

II. QUANTUM ELECTRODYNAMICS

We now turn to the quantum electrodynamic case. For absorptive dielectrics, characterized by the, in general complex, space- and frequency-dependent permittivity

$$\varepsilon(\mathbf{x},\omega) = 1 + \int_0^\infty dt\, \exp[i\omega t]\chi(\mathbf{x},t) = 1 + \hat{\chi}(\mathbf{x},\omega), \quad (2.1)$$

with $\chi(\mathbf{x},t)$ the susceptibility, the general quantized case for atoms interacting with linear absorptive dielectrics was discussed in Ref. [1]. Essential in this formalism is the introduction of two auxiliary fields, so that the combined set of electromagnetic and auxiliary fields are the solutions of equations of motion that are first order in time and no longer contain time convolutions as in the constitutive relation

$$\boldsymbol{D}(t) = \boldsymbol{E}(t) + \int_{t_0}^{t} ds \chi(t-s) \boldsymbol{E}(s), \qquad (2.2)$$

between $\boldsymbol{D}$ and $\boldsymbol{E}$. From a physical point of view the formalism describes the coupling of the vacuum electrodynamic field with a continuum of harmonic oscillators, the latter describing the material subsystem. Thus we retrieve a familiar picture, going back to Lorentz, but note that it is an exact consequence of Maxwell's equations.

The extended time evolution is unitary, which allows the introduction of a Lagrange-Hamilton formalism, which can then be quantized [5]. The Hamiltonian for the quantized fields interacting with atoms through a minimal coupling term, is given in Refs. [1,6] (we employ units such that $\varepsilon_0 = c = \hbar = 1$, m_n is the mass of the nth charge, $\mathbf{x}_n$ its coordinate, and $\mathbf{p}_n$ its momentum)

$$H = H_f + \sum_n \frac{1}{2m_n}[\mathbf{p}_n - e_n \boldsymbol{A}(\mathbf{x}_n)]^2 + V_{\text{stat}}, \qquad (2.3)$$

where

$$H_f = \sum_\beta \int d\mu \, \mu a^*(\mathbf{u}_{\mu\beta}) a(\mathbf{u}_{\mu\beta}) \qquad (2.4)$$

is the quantized Hamiltonian for the interacting electromagnetic and auxiliary fields. V_{stat} is a generalization of the potential V similar to Eq. (1.6). It is given by

$$V_{\text{stat}} = \int d\mathbf{x} \rho(\mathbf{x}) \zeta(\mathbf{x}),$$

$$- \partial_{\mathbf{x}} \cdot \varepsilon_{\text{stat}}(\mathbf{x}) \partial_{\mathbf{x}} \zeta(\mathbf{x}) = \rho(\mathbf{x})$$

$$= \sum_n e_n \delta(\mathbf{x} - \mathbf{x}_n), \qquad (2.5)$$

where $\varepsilon_{\text{stat}}(\mathbf{x}) = \varepsilon(\mathbf{x}, \omega)|_{\omega=0}$ and self-interactions are dismissed. The vector potential $\boldsymbol{A}(\mathbf{x})$ is given by

$$\boldsymbol{A}(\mathbf{x}) = \sum_\beta \int d\mu [2\mu]^{-1/2} a^*(\mathbf{u}_{\mu\beta}) \overline{\mathbf{u}_{\mu\beta 1}(\mathbf{x})} + \text{H.c.} \quad (2.6)$$

Although $\boldsymbol{A}(\mathbf{x})$ is transverse outside the dielectric, this is not the case inside; the employed gauge deviates from the Lorentz gauge [6]. The functions $\mathbf{u}_{\mu\beta}$ are eigenfunctions of a real, non-negative self-adjoint operator H_e, acting in $\mathcal{H}_e = \mathcal{H}_{\text{em}} \oplus \mathcal{H}_{\text{aux}} = L^2(\mathbb{R}^3, d\mathbf{x}; \mathbb{C}^3) \oplus \{L^2(\mathbb{R}^3, d\mathbf{x}; \mathbb{C}^3) \otimes L^2(\mathbb{R}^+, d\lambda)\}$ [1,6] and have components $\mathbf{u}_{\mu\beta 1}$ in the electric field subspace $\mathcal{H}_{\text{em}}$ and $\mathbf{u}_{\mu\beta 2}$ in the auxiliary field subspace $\mathcal{H}_{\text{aux}}$. H_e being real, the components of $\mathbf{u}_{\mu\beta}$ can be chosen real. For $\varepsilon(\mathbf{x}, \omega)$ piecewise constant in $\mathbf{x}$, the transverse and longitudinal field components are decoupled in H_f and $\boldsymbol{A}(\mathbf{x})$ [7], provided the classical fields are square integrable.

It is customary to make a long wavelength or dipole approximation, leading to the replacement $\boldsymbol{A}(\mathbf{x}_n) \rightarrow \boldsymbol{A}(\mathbf{X})$, where $\mathbf{X}$ is the atomic nuclear coordinate. But then, for $\mathbf{X}$ outside the dielectric, $\boldsymbol{A}(\mathbf{X})$ is transverse and the minimal coupling interaction does no longer give rise to an interaction between atoms and longitudinal fields, the remaining longitudinal atom-dielectric interaction being $V_{\text{stat}} - V_{\text{Coul}}$, which

leads to shifts in the atomic eigenvalues and emission spectrum but not to decay of excited atomic states through longitudinal interactions.

However, if we do not make a long wavelength approximation, the situation changes, as we shall now discuss. Thus we consider a one-electron atom with nuclear charge e and coordinate $\mathbf{X}$, which we suppose to be frozen outside the dielectric, and electronic coordinate, momentum, charge, and mass $\mathbf{x}$, $\mathbf{p}$, $-e$, and m. In the present situation, where we are dealing with V_{stat} rather than V_{Coul}, the atom still has a nondegenerate ground state. The first excited states, which are a set of degenerate s and p states in the Coulomb case, can now split up, depending on the properties of the dielectric medium.

Let the atomic ground state be φ_1 with associated eigenvalue λ_1 (the atomic eigenstates are now eigenstates in the potential V_{stat}) and suppose that at the initial time $t=0$ the system is in the state $\psi = \varphi_2 \otimes \varphi_{\text{vac}}$, φ_2 being an atomic excited state at the eigenvalue λ_2 and φ_{vac} the field vacuum state. The survival probability for the state ψ is then $W(t) = |f(t)|^2$, $t \geq 0$, where ($\Gamma = \mathbb{R} + i\delta$, $\delta > 0$)

$$f(t) = (\psi(t), \psi) = (\exp[-iHt]\psi, \psi)$$

$$= (2\pi)^{-1} \int_\Gamma dz \exp[-izt]([z-H]^{-1}\psi, \psi). \qquad (2.7)$$

Here $(f, g) = \langle g | f \rangle$ is the inner product of states f and g. Then, if $([z-H]^{-1}\psi, \psi)$ has an analytic extension in the lower complex half plane $\mathbb{C}^-$ with poles in $z_j = \omega_j - i\gamma_j \in \mathbb{C}^-$, the corresponding pole contributions give rise to decaying terms in $f(t)$, proportional to $\exp[-2\gamma_j t]$. In Refs. [5,6] we used the Feshbach formula to obtain the leading order contribution to γ_j. In Ref. [6] we used the interaction $\frac{e}{m}\mathbf{p} \cdot \boldsymbol{A}(\mathbf{X})$ but, as we have noted above, this is not sufficiently accurate for longitudinal decay. Thus we employ

$$H_{\text{mf}} = \frac{e}{2m}\{\mathbf{p} \cdot \boldsymbol{A}(\mathbf{x}) + \boldsymbol{A}(\mathbf{x}) \cdot \mathbf{p}\}. \qquad (2.8)$$

Now using the Feshbach formalism (for details see Appendix A) we find that the eigenvalue λ_2 acquires a negative imaginary contribution γ, which, to leading order, is given by

$$\gamma = \gamma(\omega_0) = \frac{i}{2}\left(\frac{e}{2m}\right)^2 \int d\mathbf{x} d\mathbf{y} \overline{\mathbf{g}(\mathbf{x})} \cdot \langle \mathbf{x} | \mathsf{R}_e(z) - \mathsf{R}_e^*(z) | \mathbf{y} \rangle \cdot \mathbf{g}(\mathbf{y})$$

$$= \frac{i}{2}\left(\frac{e}{2m}\right)^2 (\{\mathsf{R}_e(z) - \mathsf{R}_e^*(z)\}\mathbf{g}, \mathbf{g}), \qquad (2.9)$$

where $z^2 = \omega_0^2 + i0$ with $\omega_0 = \lambda_2 - \lambda_1$ the atomic transition frequency and (recall that U is the unit 3×3 matrix)

$$\mathsf{R}_e(z) = [z^2 \varepsilon(\mathbf{x}, z) - \mathsf{h}]^{-1},$$

$$\mathsf{h} = -\partial_{\mathbf{x}}^2 \mathsf{U} + \partial_{\mathbf{x}}\partial_{\mathbf{x}} = \mathbf{p}^2 \mathsf{U} - \mathbf{pp}, \quad \mathbf{p} = -i\partial_{\mathbf{x}},$$

$$\mathbf{g}(\mathbf{x}) = \partial_{\mathbf{r}}\overline{\varphi_1(\mathbf{r}, \mathbf{X})}\varphi_2(\mathbf{r}, \mathbf{X}) - \overline{\varphi_1(\mathbf{r}, \mathbf{X})}\partial_{\mathbf{r}}\varphi_2(\mathbf{r}, \mathbf{X}),$$

$$\mathbf{r} = \mathbf{x} - \mathbf{X}. \qquad (2.10)$$

Here $\mathsf{R}_e(z)$, the component in $\mathcal{H}_{em}$ of the operator $[z^2 - \mathsf{H}_e]^{-1}$, is the inverse of the Helmholtz operator:

$$\mathsf{R}_e(z) = ([z^2 - \mathsf{H}_e]^{-1})_{11} = [z^2 \varepsilon(\mathbf{x}, z) - \mathsf{h}]^{-1}. \qquad (2.11)$$

In the piecewise constant case [7], $\mathsf{R}_e(z)$ decomposes into longitudinal and transverse parts

$$\mathsf{R}_e(z) = R^{\parallel}(z)\mathsf{P}^{\parallel} + R^{\perp}(z)\mathsf{P}^{\perp},$$

$$R^{\parallel}(z) = [z^2 \varepsilon(\mathbf{x}, z)]^{-1},$$

$$R^{\perp}(z) = [z^2 \varepsilon(\mathbf{x}, z) - \mathbf{p}^2]^{-1}, \qquad (2.12)$$

where $\mathsf{P}^{\parallel}$ and $\mathsf{P}^{\perp}$ are the projector upon the longitudinal and transverse subspaces [see Eq. (1.2)]. Hence γ decomposes as

$$\gamma = \gamma^{\parallel} + \gamma^{\perp}. \qquad (2.13)$$

Below we denote by $R(\omega_0)$ the operator $R(\omega_0 + i0)$. We now study both contributions in some detail.

A. The longitudinal case

We have

$$\gamma^{\parallel} = \left(\frac{e}{2m\omega_0}\right)^2 \langle \mathbf{g} | \cdot \frac{\operatorname{Im} \varepsilon(\mathbf{x}, \omega_0)}{|\varepsilon(\mathbf{x}, \omega_0)|^2} \mathsf{P}^{\parallel} \cdot |\mathbf{g}\rangle$$

$$= \left(\frac{e}{2m\omega_0}\right)^2 \left(\frac{\operatorname{Im} \chi(\mathbf{x}, \omega_0)}{|\varepsilon(\mathbf{x}, \omega_0)|^2} \mathbf{g}^{\parallel}, \mathbf{g}^{\parallel}\right). \qquad (2.14)$$

In the piecewise constant case $\varepsilon(\mathbf{x}, \omega_0)$ and $\mathsf{P}^{\parallel}$ commute, so

$$\gamma^{\parallel} = \left(\frac{e}{2m\omega_0}\right)^2 \langle \mathbf{g} | \cdot \frac{\operatorname{Im} \chi(\mathbf{x}, \omega_0)^{1/2}}{|\varepsilon(\mathbf{x}, \omega_0)|} \mathsf{P}^{\parallel} \frac{\operatorname{Im} \chi(\mathbf{x}, \omega_0)^{1/2}}{|\varepsilon(\mathbf{x}, \omega_0)|} \cdot |\mathbf{g}\rangle$$

$$\leqslant \left(\frac{e}{2m\omega_0}\right)^2 \langle \mathbf{g} | \frac{\operatorname{Im} \varepsilon(\mathbf{x}, \omega_0)}{|\varepsilon(\mathbf{x}, \omega_0)|^2} | \mathbf{g}\rangle \qquad (2.15)$$

Note that here $\varepsilon = \varepsilon(\omega_0)$ is taken at the atomic transition frequency ω_0 and not at $\omega = 0$ as in V_{stat}. From Eq. (2.14) we conclude that $\gamma^{\parallel}$ can be nonvanishing if there is overlap between the atomic wave functions and the dielectric. If the latter is confined to the half space $x_3 < 0$ and with $\mathbf{X} = X\mathbf{e}_3$, $X > 0$, then

$$\varepsilon(\mathbf{x}, \omega_0) = 1 + \chi(\omega_0)\theta(-x_3) = 1 + \chi(\omega_0)\theta(-r_3 - X) \qquad (2.16)$$

and we have

$$\gamma^{\parallel}(X) \leqslant \left(\frac{e}{2m\omega_0}\right)^2 \frac{\operatorname{Im} \chi(\omega_0)}{1 + |\chi(\omega_0)|^2 + 2\operatorname{Re} \chi(\omega_0)}$$

$$\times \int_{-\infty}^{+\infty} dr_1 dr_2 \int_{-\infty}^{-X} dr_3 |\mathbf{g}(\mathbf{r})|^2. \qquad (2.17)$$

Since the atomic eigenfunctions decay exponentially on an atomic scale, the same holds true for $\gamma^{\parallel}(X)$.

Let us see what happens in the dipole approximation. Thus we replace Eq. (2.9) by

$$\gamma^{\parallel}_{dip} = \frac{i}{2}\left(\frac{e}{2m}\right)^2 \int d\mathbf{x}d\mathbf{y}\overline{\mathbf{g}^{\parallel}(\mathbf{x})} \cdot \langle \mathbf{X} | \mathsf{R}_e(\omega_0) - \mathsf{R}_e^{*}(\omega_0) | \mathbf{X} \rangle$$

$$\cdot \mathbf{g}^{\parallel}(\mathbf{y}) = \frac{i}{2}\omega_0^2 \mathbf{d}^{\parallel} \cdot \langle \mathbf{X} | R^{\parallel}(\omega_0) - R^{\parallel}(\omega_0)^{*} | \mathbf{X} \rangle \cdot \overline{\mathbf{d}}^{\parallel},$$

$$(2.18)$$

where, noting that $\partial_{\mathbf{r}}\varphi_j = -i\mathbf{p}\varphi_j$ and $\mathbf{p} = im[H_{at}, \mathbf{r}]$,

$$\mathbf{d} = e \int d\mathbf{x}\mathbf{x}\varphi_1(\mathbf{x})\overline{\varphi_2(\mathbf{x})} = -\frac{e}{2m\omega_0}\int d\mathbf{x}\overline{\mathbf{g}(\mathbf{x})} = \mathbf{d}^{\parallel} + \mathbf{d}^{\perp},$$

$$\mathbf{d}^{\parallel} = -\frac{e}{2m\omega_0}\int d\mathbf{x}\overline{\mathbf{g}^{\parallel}(\mathbf{x})},$$

$$\mathbf{d}^{\perp} = -\frac{e}{2m\omega_0}\int d\mathbf{x}\overline{\mathbf{g}^{\perp}(\mathbf{x})}. \qquad (2.19)$$

However, $\gamma^{\parallel}_{dip}$ does not exist since $\langle \mathbf{X} | R^{\parallel}(\omega_0) | \mathbf{X} \rangle = \langle \mathbf{X} | [\omega_0^2 \varepsilon(\mathbf{X}, \omega_0)]^{-1} | \mathbf{X} \rangle$ is infinite. However, in Eq. (2.18) two infinite quantities are subtracted, so the result may be finite. Indeed, if we approximate Eq. (2.14) by replacing $\varepsilon(\mathbf{x}, \omega_0)$ by $\varepsilon(\mathbf{X}, \omega_0)$,

$$\gamma^{\parallel} \rightarrow \left(\frac{e}{2m\omega_0}\right)^2 \frac{\operatorname{Im} \varepsilon(\mathbf{X}, \omega_0)}{|\varepsilon(\mathbf{X}, \omega_0)|^2} \langle \mathbf{g} | \cdot \mathsf{P}^{\parallel} \cdot |\mathbf{g}\rangle$$

$$= \left(\frac{e}{2m\omega_0}\right)^2 \frac{\operatorname{Im} \varepsilon(\mathbf{X}, \omega_0)}{|\varepsilon(\mathbf{X}, \omega_0)|^2} \langle \mathbf{g} | \cdot \mathbf{p}\frac{1}{\mathbf{p}^2}\mathbf{p} \cdot |\mathbf{g}\rangle$$

$$= e^2 \frac{\operatorname{Im} \varepsilon(\mathbf{X}, \omega_0)}{|\varepsilon(\mathbf{X}, \omega_0)|^2} \langle \overline{\varphi_1\varphi_2} | \frac{1}{\mathbf{p}^2} | \overline{\varphi_1\varphi_2} \rangle \qquad (2.20)$$

which is finite but vanishes for $\mathbf{X}$ outside the dielectric.

B. The transverse case

Let us compare the above results with the transverse situation. Now, with $\mathbf{g}^{\perp}$ the transverse component of $\mathbf{g}$,

$$\gamma^{\perp} = \frac{i}{2}\left(\frac{e}{2m}\right)^2 (\{R^{\perp}(\omega_0) - R^{\perp}(\omega_0)^{*}\}\mathbf{g}^{\perp}, \mathbf{g}^{\perp}). \qquad (2.21)$$

Except for special cases such as certain rotational invariant systems, the Green's function associated with $R^{\perp}(z)$ cannot be obtained explicitly. Instead we consider the approximate case where $\operatorname{Im} \varepsilon(\mathbf{x}, \omega_0) = \operatorname{Im} \chi(\mathbf{x}, \omega_0)$ is retained to first order. Thus we split $\varepsilon(\mathbf{x}, \omega_0)$ into its real and imaginary parts

$$\varepsilon(\mathbf{x}, \omega_0) = \operatorname{Re} \varepsilon(\mathbf{x}, \omega_0) + i \operatorname{Im} \varepsilon(\mathbf{x}, \omega_0) = \operatorname{Re} \varepsilon(\mathbf{x}, \omega_0)$$

$$+ i \operatorname{Im} \chi(\mathbf{x}, \omega_0), \qquad (2.22)$$

and by only keeping terms to first order in $\operatorname{Im} \varepsilon(\mathbf{x}, \omega_0) = \operatorname{Im} \chi(\mathbf{x}, \omega_0)$ in $R^{\perp}(\omega_0) - R^{\perp}(\omega_0)^{*}$ we obtain

$$\gamma^{\perp} = \gamma_1^{\perp} + \gamma_2^{\perp},$$

$$\gamma_1^{\perp} = \frac{i}{2}\left(\frac{e}{2m}\right)^2 (\{R_1^{\perp}(\omega_0) - R_1^{\perp}(\omega_0)^{*}\}\mathbf{g}^{\perp}, \mathbf{g}^{\perp}),$$

$$\gamma_2^{\perp} = \frac{1}{2}\left(\frac{e\omega_0}{2m}\right)^2 (R_1^{\perp}(\omega_0)^* \mathrm{Im}\, \chi(\mathbf{x},\omega_0) R_1^{\perp}(\omega_0)\mathbf{g}^{\perp}, \mathbf{g}^{\perp}),$$

$$(2.23)$$

where

$$R_1^{\perp}(z) = [z^2 \, \mathrm{Re}\, \varepsilon(\mathbf{x},z) - \mathbf{p}^2]^{-1}. \qquad (2.24)$$

Note that $\gamma_1^{\perp}$ is the decay constant for the nonabsorptive but dispersive system characterized by the real dielectric function $\mathrm{Re}\, \varepsilon(\mathbf{x},\omega)$. We can rewrite it as

$$\gamma_1^{\perp} = \pi\left(\frac{e}{2m}\right)^2 \left(\delta(\omega_0^2 \, \mathrm{Re}\, \varepsilon(\mathbf{x},\omega_0) - \mathbf{p}^2)\mathbf{g}^{\perp}, \mathbf{g}^{\perp}\right)$$

$$= \pi\left(\frac{e}{2m}\right)^2 \left[\delta(\omega_0^2 \, \mathrm{Re}\, \varepsilon(\mathbf{x},\omega_0) - \mathbf{p}^2)\mathsf{P}^{\perp}\mathbf{g}, \mathbf{g}\right]$$

$$= \pi\left(\frac{e}{2m}\right)^2 \int d\mathbf{x} \int d\mathbf{y} \overline{\mathbf{g}(\mathbf{x})}$$

$$\times \langle \mathbf{x} | \delta(\omega_0^2 \, \mathrm{Re}\, \varepsilon(\mathbf{x},\omega_0) - \mathbf{p}^2)\mathsf{P}^{\perp} | \mathbf{y}\rangle \cdot \mathbf{g}(\mathbf{y}). \quad (2.25)$$

We obtain the dipole approximation by replacing $\langle \mathbf{x} | \delta(\omega_0^2 \, \mathrm{Re}\, \varepsilon(\mathbf{x},\omega_0) - \mathbf{p}^2)\mathsf{P}^{\perp} | \mathbf{y}\rangle$ by

$$\langle \mathbf{X} | \delta(\omega_0^2 \, \mathrm{Re}\, \varepsilon(\mathbf{X},\omega_0) - \mathbf{p}^2)\mathsf{P}^{\perp} | \mathbf{X}\rangle$$

$$= \int d\mathbf{k} \langle \mathbf{X} | \mathbf{k}\rangle \delta(\omega_0^2 \, \mathrm{Re}\, \varepsilon(\mathbf{X},\omega_0) - k^2)\{\mathsf{U} - \mathbf{e_k}\mathbf{e_k}\}\langle \mathbf{k} | \mathbf{X}\rangle$$

$$= (2\pi)^{-3} \int d\mathbf{k}\, \delta(\omega_0^2 \, \mathrm{Re}\, \varepsilon(\mathbf{X},\omega_0) - \mathsf{k}^2)\{\mathsf{U} - \mathbf{e_k}\mathbf{e_k}\}$$

$$= (2\pi)^{-3}\frac{2}{3}\mathsf{U} \int d\mathbf{k}\, \delta(\omega_0^2 \, \mathrm{Re}\, \varepsilon(\mathbf{X},\omega_0) - k^2)$$

$$= \frac{\omega_0}{6\pi^2}\sqrt{\mathrm{Re}\, \varepsilon(\mathbf{X},\omega_0)}\mathsf{U}, \qquad (2.26)$$

so, using Eq. (2.19),

$$\gamma_{1\mathrm{dip}}^{\perp} = \pi\left(\frac{e}{2m}\right)^2 \int d\mathbf{x}\overline{\mathbf{g}(\mathbf{x})}\frac{\omega_0}{6\pi^2}\sqrt{\mathrm{Re}\, \varepsilon(\mathbf{X},\omega_0)}\mathsf{U} \cdot \int d\mathbf{y}\mathbf{g}(\mathbf{y})$$

$$= \frac{\omega_0^3}{6\pi}\sqrt{\mathrm{Re}\, \varepsilon(\mathbf{X},\omega_0)}|\mathbf{d}|^2. \qquad (2.27)$$

In the vacuum case $\sqrt{\mathrm{Re}\, \varepsilon(\mathbf{X},\omega_0)}$ is replaced by 1 and we retrieve the decay constant $\Gamma_{\mathrm{vac}} = 2\gamma_{1\mathrm{dip}}^{\perp} = \omega_0^3|\mathbf{d}|^2/(3\pi)$ for an atom in free space. Here we assumed that $\mathrm{Re}\, \varepsilon(\mathbf{x},\omega_0) \geq 0$. This is not always the case. For small silver spheres, which otherwise behave as an absorbing dielectric, $\mathrm{Re}\, \varepsilon(\mathbf{x},\omega_0)$ can be negative in a frequency interval in the optical range, resulting in $\gamma_1^{\perp}(\omega_0) = 0$. In the half-space case, with $\mathbf{X}$ outside the dielectric, the above expression reduces to the vacuum case. Another interesting situation is that of periodic dielectrics (photonic crystals). Then it can happen that ω_0 falls in a photonic band gap and $\gamma_1^{\perp}$ vanishes. But this need not be the case for $\gamma_2^{\perp}$.

Comparing $\gamma_2^{\perp}$ with $\gamma^{\|}$ we see that apart from the obvious change $\mathbf{g}^{\|} \to \mathbf{g}^{\perp}$ the only difference is that $R^{\|}(\omega_0)$ is replaced by $R_1^{\perp}(\omega_0)$. However, this change is rather profound.

Whereas $R^{\|}(\omega_0)$ is a multiplication operator in coordinate space, due to the presence of $\mathbf{p}^2$ in $R_1^{\perp}(\omega_0)$, this operator is nonlocal in coordinate space and leads to wave propagation. Thus we expect a different behavior, in fact some power law, as the atom is moved away from the dielectric. We demonstrate this, making the further approximation of replacing $R_1^{\perp}(z)$ in Eq. (2.23) by its free counterpart

$$R_0^{\perp}(z) = [z^2 - \mathbf{p}^2]^{-1}, \qquad (2.28)$$

taking for φ_1 and φ_2 hydrogenic $1s$ and $2p$ states, solely depending on the atomic internal coordinate $\mathbf{r}$. This approximation is not unreasonable for a sufficiently large distance between the atom and dielectric [from a mathematical point of view $R^{\perp}(z)$ and $R_1^{\perp}(z)$ converge towards $R_0^{\perp}(z)$ in strong resolvent sense as $X \to \infty$]. However, contrary to the original Eq. (2.21), the approximate expression, Eq. (2.23) for $\gamma_2^{\perp}$ in general only exists for $\mathrm{Im}\, \chi(\mathbf{x},\omega_0)$ restricted to a bounded space region. It becomes infinite in the half space case. However for a sphere centered in the origin and taking Coulomb $1s$ and $2p$ states for the φ's we find that $\gamma_2^{\perp}$, which is now finite, contains a contribution proportional to X^{-2} for large X and additional terms featuring higher powers of X^{-2} and a contribution that is exponentially decaying on an atomic scale

$$\gamma_2^{\perp}(\mathbf{X}) \overset{X \to \infty}{\sim} X^{-2} + O(X^{-4}). \qquad (2.29)$$

The decay parameter in the exponential contribution is the same as in the corresponding longitudinal case. Details are given in Appendix B.

III. THE JENA FORMALISM

As mentioned earlier the Hamiltonian employed by the Jena group [3] differs from the one in Ref. [1]. In particular it involves V_{Coul} rather than V_{stat}. Also the vector potential has no longitudinal component but there is an additional term of the nature of a scalar potential, involving longitudinal field operators. On the other hand, as shown in Ref. [1], a unitary transformation exists (alternatively the same result follows by adding a suitable total time derivative to the Lagrangean), that relates H, above, to one that features the Coulomb potential and a scalar potential as in Ref. [3] (in fact we are dealing with a gauge transformation of the vector and scalar potentials). The two do not coincide since in Ref. [3] the special case of an infinitely extended absorptive dielectric is considered, in which case the electromagnetic fields become functionals of the auxiliary ones [1]. We now show directly that the Hamiltonian used in Ref. [3] is unitarily equivalent to one that once more contains V_{stat}.

Starting point in the Jena formalism is a set of creation and annihilation operators $\mathbf{f}^*(\mathbf{x},\omega)$ and $\mathbf{f}(\mathbf{x},\omega)$, $\omega \geq 0$, acting in the symmetric Fock space over $L^2(\mathbb{R}^3, d\mathbf{x}; \mathbb{C}^3)$ and satisfying

$$[\mathbf{f}(\mathbf{x}_1,\omega_1), \mathbf{f}^*(\mathbf{x}_2,\omega_2)] = \delta(\mathbf{x}_1 - \mathbf{x}_2)\delta(\omega_1 - \omega_2)\mathsf{U}. \quad (3.1)$$

The fields are then given by (we set $\hbar = c = \varepsilon_0 = 1$)

$$\boldsymbol{E}(\mathbf{x}) = \int_0^{\infty} d\omega\{\boldsymbol{E}(\mathbf{x},\omega) + \boldsymbol{E}^*(\mathbf{x},\omega)\},$$

$$A(\mathbf{x}) = \int_0^\infty d\omega \frac{1}{i\omega} \{E(\mathbf{x},\omega) - E^*(\mathbf{x},\omega)\},$$

$$E(\mathbf{x},\omega) = \frac{i\omega^2}{\sqrt{\pi}} \int d\mathbf{y} \mathsf{G}(\mathbf{x},\mathbf{y},\omega) \cdot \sqrt{\mathrm{Im}\,\varepsilon(\mathbf{y},\omega)} \mathbf{f}(\mathbf{y},\omega),$$

$$(3.2)$$

where G is the Helmholtz Green's function

$$\mathsf{G}(\mathbf{x},\mathbf{y},\omega) = \mathsf{G}(\mathbf{x},\mathbf{y},\omega = i0) = -\langle\mathbf{x}|[z^2\varepsilon(\mathbf{x},z) - \mathsf{h}]^{-1}|\mathbf{y}\rangle|_{z=\omega+i0}$$
$$= -\langle\mathbf{x}|\mathsf{R}_e(\omega + i0)|\mathbf{y}\rangle|,$$

$$\mathsf{h} = \partial_\mathbf{x} \times (\partial_\mathbf{x} \times \cdots) = \mathbf{p}^2\mathsf{U} - \mathbf{p}\mathbf{p}, \quad \mathbf{p} = -i\partial_\mathbf{x}. \quad (3.3)$$

The Hamiltonian employed in Ref. [3] is then

$$H = H_f + \sum_n \frac{1}{2m_n}[\mathbf{p}_n - e_n A^\perp(\mathbf{x}_n)]^2 + V_{\mathrm{Coul}} + (\rho,\varphi),$$

$$H_f = \int d\mathbf{x} \int_0^\infty d\omega \omega \mathbf{f}^*(\mathbf{x},\omega) \cdot \mathbf{f}(\mathbf{x},\omega), \quad -\partial_\mathbf{x}\varphi(\mathbf{x}) = E^\parallel(\mathbf{x}).$$

$$(3.4)$$

Let now

$$\mathbf{W}(\mathbf{x}) = \mathbf{W}(\mathbf{x},\mathbf{x}_1,\mathbf{x}_2,\dots) = \partial_\mathbf{x}\zeta_0(\mathbf{x},\mathbf{x}_1,\mathbf{x}_2,\dots),$$

$$\zeta_0(\mathbf{x},\mathbf{x}_1,\mathbf{x}_2,\dots) = \sum_n \frac{e_n}{4\pi|\mathbf{x} - \mathbf{x}_n|}, \quad (3.5)$$

and U the unitary operator

$$U = \exp[i(A^\parallel,\mathbf{W})] = \exp[i(A,\mathbf{W})],$$

$$(\mathbf{F},\mathbf{G}) = \int d\mathbf{x}\mathbf{F}(\mathbf{x})\overline{\mathbf{G}(\mathbf{x})}. \quad (3.6)$$

We define

$$H' = UHU^{-1}. \quad (3.7)$$

Then

$$H' = H_f + \sum_n \frac{1}{2m_n}[\mathbf{p}_n - A(\mathbf{x}_n)]^2 + V_{\mathrm{stat}}, \quad (3.8)$$

with V_{stat} given by Eq. (2.5). Thus the term (ρ,φ) has disappeared, V_{Coul} is replaced by V_{stat} and $A^\parallel$ is added to $A^\perp$. We note that H' is similar to Eq. (2.3). The proof is given in Appendix C.

IV. DISCUSSION

A. Summary of results

We studied the longitudinal interactions between an atom and an absorptive dielectric and distinguished two aspects. The first, and probably the most interesting, is the appearance of V_{stat}, which involves the static permittivity $\varepsilon_{\mathrm{stat}}$

$=\varepsilon(\omega=0)$, instead of the Coulomb potential. It is an exact consequence of the employed formalism and can be traced back to the fact that the null space of the generator of the time evolution in the auxiliary field formalism only contains a subset of the longitudinal subspace, a property it shares with H_e. A remnant of this we find in Eq. (C17) below, where Q_e does not equal the projector upon the transverse subspace. V_{stat} gives rise to a shift in the atomic eigenvalues relative to the Coulomb case.

There is a direct way to see that $\varepsilon_{\mathrm{stat}}$ enters into the time evolution. To see this, we write

$$E(t) = (2\pi)^{-1}\int_\Gamma dz \exp[-izt]\hat{E}(z),$$

$$\Gamma = \mathbb{R} + i\delta, \quad \delta > 0, \quad (4.1)$$

where $\hat{E}(z)$, the Laplace transform of $E(t)$, can be expressed, using Maxwell's equations, in terms of the initial fields at $t=0$ and $\hat{J}(z)$, the Laplace transform of the current density

$$J(\mathbf{x},t) = \sum_n e_n\dot{\mathbf{x}}_n(t)\delta(\mathbf{x} - \mathbf{x}_n(t)), \quad (4.2)$$

i.e.,

$$\hat{E}(z) = [z^2\varepsilon(\mathbf{x},z) - \mathsf{h}]^{-1}[iz\{E(0) - \hat{J}(z)\} - \partial_\mathbf{x} \times B(0)].$$

$$(4.3)$$

The right-hand side has a pole in $z=0$. Its residue can easily be calculated using the auxiliary field formalism, but also by directly determining the asymptotic form of $[z^2\varepsilon(\mathbf{x},z) - \mathsf{h}]^{-1}$ as $z\to 0$ (see Ref. [8], Appendix A), with corresponding contribution to $E(t)$,

$$E_0(\mathbf{x},t) = -\partial_\mathbf{x}\zeta(\mathbf{x},t),$$

$$-\partial_\mathbf{x} \cdot \varepsilon_{\mathrm{stat}}(\mathbf{x})\partial_\mathbf{x}\zeta(\mathbf{x},t) = \rho(\mathbf{x},t) = \sum_n e_n\delta(\mathbf{x} - \mathbf{x}_n(t)).$$

$$(4.4)$$

Laplace transforms can also be used to obtain an expression for $A^\parallel(\mathbf{x},t)$ for $\mathbf{x}$ inside the dielectric. In the special case, where an external (i.e., outside the dielectric) time-dependent charge distribution $\rho(\mathbf{x},t)$ is switched on at $t=0$, at which time the fields vanish, we can start from the Laplace transform of $\partial_\mathbf{x} \cdot D(\mathbf{x},t) = \rho(\mathbf{x},t)$ to obtain

$$A^\parallel(\mathbf{x},t) = \partial_\mathbf{x}\int d\mathbf{y}\frac{1}{4\pi|\mathbf{x} - \mathbf{y}|}\int_0^t ds m(\mathbf{x},t - s)\rho(\mathbf{y},s),$$

$$m(\mathbf{x},t) = \frac{1}{2\pi i}\int d\omega \exp[-i\omega t]\frac{1}{\omega}\left\{\frac{1}{\varepsilon_{\mathrm{stat}}(\mathbf{x})} - \frac{1}{\varepsilon(\mathbf{x},\omega)}\right\}.$$

$$(4.5)$$

Note that the integrand in the last equation is well behaved in $\omega=0$ since $\varepsilon_{\mathrm{stat}}=\varepsilon(\omega=0)$. Thus $A^\parallel(\mathbf{x},t)$ vanishes for $\mathbf{x}$ outside the dielectric, where $\varepsilon_{\mathrm{stat}}(\mathbf{x})=\varepsilon(\mathbf{x},\omega)=1$, but depends on the difference of their inverses inside the medium.

Another aspect is a coupling between the atom and the longitudinal field modes, which turns the excited atomic states into resonances (they acquire a negative imaginary part), giving rise to the decay of excited atomic states. Contrary to radiative decay, this mechanism requires the close proximity of the atom and absorptive medium and is absent for an atom outside the medium in the dipole approximation. The decay parameter $\gamma^\|$ involves $\varepsilon(\omega_0)$, where ω_0 is the atomic transition frequency and vanishes exponentially on an atomic scale with increasing distance between the atom and absorptive dielectric.

Let us return to the potential (1.5), which we write as

$$V = V_{\text{Coul}} + \frac{\chi}{2+\chi}\left\{\frac{e^2}{4\pi|\mathbf{r}+2\mathbf{X}|} - \frac{e^2}{8\pi|r_3+X|}\right\}, \quad (4.6)$$

which is valid for a hydrogen atom with fixed nucleus at $\mathbf{X}=X\mathbf{e}_3$ in vacuum above the half space $x_3 < 0$, filled with a spatially homogeneous absorptive dielectric with susceptibility χ. Here $\mathbf{r}=\mathbf{x}-\mathbf{X}$ is the distance between the electron and proton. For large χ (for water at $0\,^\circ$C the static permittivity is 87.9, for ice at the same temperature 96.6) $\chi/(2+\chi)\approx 1$ and for an atom close to the interface there may be observable effects on the atomic eigenvalues and radiative emission spectrum. In principle the corrections to the Coulomb eigenvalues can be calculated for the hydrogenic case. For an atom close to the interface $\mathbf{r}$ and $\mathbf{X}$ are of the same order, so an expansion based upon relative smallness of r and X is not useful. In addition other, more complicated, atoms are used in practice.

Other processes may change as well. In particular resonant energy transfer between identical atoms can be affected. For instance Förster processes [9,10] can be such a case. They are usually treated by means of a dipole model for the atoms and in the interactions between them the vacuum permittivity is replaced by the permittivity of the embedding material taken at the atomic transition frequency ω_0. The argument behind this is that the excited atom is associated with an oscillating charge distribution with frequency ω_0. If the dielectric does not have eigenvalues or resonances near ω_0 (if this were the case it would be strongly absorbing), then the effect would be a dynamic polarization of the medium, which involves $\varepsilon(\mathbf{x},\omega_0)$.

Results by the Jena group [3] and the author (Ref. [1], Sec. VIII), again based upon a quantized form of the phenomenological Maxwell's equations, also show an ω_0 dependence, but now through the Helmholtz Green's function. Here the dipole approximation was made. A more precise description, using the present approach, leads to a more complicated situation. Now the atomic eigenvalues of atom j depend not only on the relative electron coordinate $\mathbf{r}_j$ with respect to the nuclear coordinate $\mathbf{X}_j$ but, since V_{stat} depends on the latter, also on $\mathbf{X}_j$ itself. Thus, if two atoms are in regions with different permittivity, their transition frequencies may also differ, thus modifying or even destroying the resonance condition.

In an essentially infinite medium, containing a collection of embedded atoms, Förster processes can contribute to the broadening of individual atomic levels in addition to radia-

tive broadening. In practice it is difficult to disentangle the two [11].

Apart from an imaginary component, the coupling to longitudinal fields also give a shift in the atomic eigenvalues. Thus, in Sec. II, $\lambda_2 \rightarrow \lambda_2 + \Delta\lambda_2$ with

$$\Delta\lambda_2^\| = \left(\frac{e}{2m}\right)^2 \int_0^\infty d\mu \frac{1}{2\mu}\frac{1}{\omega_0 + i\delta - \mu}$$

$$\times \langle \mathbf{g}| \cdot \frac{\text{Im}\,\varepsilon(\mathbf{x},\mu)}{\pi\mu|\varepsilon(\mathbf{x},\mu)|^2}\mathsf{P}^\| \cdot |\mathbf{g}\rangle. \quad (4.7)$$

We already encountered its imaginary part $\gamma^\|$. However, as can be seen from inserting a Lorentz susceptibility

$$\varepsilon(\mathbf{x},\mu) \sim 1 - \frac{\Omega^2}{\mu(\mu + i\Gamma)}, \quad (4.8)$$

we have an infrared diverging (nonintegrable in $\mu=0$) real part (Lamb shift). This is well known from the vacuum case but there the fields are transverse. But here it is of a different nature since it depends on the behavior of $\text{Im}\,\varepsilon(\mathbf{x},\mu)$ in $\mu=0$. Thus, if $\text{Im}\,\varepsilon(\mathbf{x},\mu)=\mathcal{O}(\mu^{1+\delta})$, $\delta > 0$, as $\mu\downarrow 0$, then $\Delta\lambda_2^\|$ is finite. In general the renormalization procedure discussed in [5] for nonabsorptive dielectrics, although it applies to the transverse case, does not work in the longitudinal situation.

The above results are obtained using a quantized form of the phenomenological Maxwell's equations. However, it should be realized that the effects discussed above take place on a scale of the order of atomic dimensions, where the validity of the macroscopic equations becomes questionable. We also assumed that the atomic nucleus is frozen in a position close to but outside the absorptive dielectric. This can be accomplished in practice by embedding the atom in a second dielectric, nonabsorbing and nondispersive in the frequency range of interest. For atoms inside dielectrics the phenomenological Maxwell's equations are in principle no longer applicable. The interactions with an atom with its nearest neighbors will not be described accurately in this way. Sometimes this situation is treated using a real cavity model. See, for instance, Ref. [12]. There the atom is assumed to be contained in a small vacuum sphere inside the dielectric. Its radius is then chosen to obtain the best possible results. Since the atom is now in vacuum, the usual minimal coupling featuring the microscopic vector potential is employed. From a microscopic point of view this should be correct if there is no significant overlap with the wave function of the dielectric, typically for distances of a few atomic diameters or more. Note further that the real cavity model leads to boundary conditions, modifying the transverse Helmholtz Green's function and hence radiative lifetimes, but that in the longitudinal Green's function, which does not contain differential operators, no boundary conditions are involved, only changes in $\varepsilon(\mathbf{x},\omega_0)$ and $\varepsilon_{\text{stat}}(\mathbf{x})$ appear. A thorough discussion of the electrodynamics of mesoscopic media is given by Keller [13]. In concluding this part we note that the phenomenological approach gives some insight into the processes that take place but that suitable experiments, if possible, should be useful to learn more about the actual situation.

B. Microscopic description of longitudinal decay

Radiative atomic decay is well understood. It is due to the coupling of the atomic states with the field continuum states, which already takes place in vacuum. There, to leading order, the decay constant is proportional to the field local density of states, which is given by the imaginary part of the Helmholtz Green's function, taken at the atomic nuclear coordinates. The latter is still true in the transverse absorptive case although the density of states concept breaks down (see Ref. [14] for the photonic crystal case). In the longitudinal situation we also expect some coupling to a continuum but here the situation is less obvious, longitudinal decay being absent in the vacuum case.

In a microscopic description the dielectric material can be interpreted as a large molecule and the Coulomb gauge can be employed. Then decay of an excited atom through longitudinal interactions must be caused by a coupling, through Coulomb interactions, with continuum modes in the spectrum of the material. Apart from electron detachment from the material (such as the photoelectric effect in metals, not considered here), this, in general, requires an infinitely extended dielectric. For instance, atoms can then couple to a continuous phonon spectrum. Such processes seem quite unlikely, suggesting that longitudinal decay hardly takes place (but the situation changes drastically if vibrationally excited molecules are considered). Experimental verification may be difficult due to other decay modes such as radiative decay.

Dielectric systems interacting with transverse fields have been studied from a mesoscopic point of view in the past (the well-known Hopfield model [15,16]) for spatially homogeneous systems. For an extension to dielectrics filling a half space, see Ref. [17].

C. The unitary transformation U

Although a unitary transformation such as $U = \exp[i(\boldsymbol{A}, \mathbf{W})]$, Eq. (3.6), leaves the spectrum, and in particular the eigenvalues, of H invariant, this is not necessarily true for the resonances originating from the excited atomic states due to the coupling with the fields. Note here that

$$([z-H]^{-1}\varphi, \varphi) = ([z-H']^{-1}U\varphi, U\varphi), \qquad (4.9)$$

so, if $\varphi = \varphi_{at} \otimes \varphi_{\text{vac}}$, $U\varphi$ will contain contributions from all Fock layers, whereas the atomic state is also altered,

$$U\varphi = \varphi + i(\boldsymbol{A}, \mathbf{W})\varphi + \cdots, \qquad (4.10)$$

and the contributions from resonant poles on both sides of Eq. (4.9) look quite different. For further remarks, see Ref. [1], Sec. X. Strictly speaking U is not properly defined since the vector potential has an infrared divergence. This can be remedied in an *ad hoc* way by introducing a cutoff in $\boldsymbol{A}$, but here this is not necessary.

Another point is that U does not have a proper limit in the dipole approximation. Formally, for a one electron system (nuclear coordinate $\mathbf{X}$, charge $-e$, relative electron coordinate $\mathbf{r}$) it turns into $U_{\text{dip}} = \exp[i e \mathbf{r} \cdot A^{\parallel}(\mathbf{X})]$. Although the momenta transform correctly, infinities are encountered in calculating the transformed field Hamiltonian. In particular Eq. (C13) now diverges and this remains true with a cutoff in the vector potential. But it remains possible to make a dipole expansion of V_{stat} in the final result. For example, we can do so for the potential (4.6).

D. Related work

Atoms interacting with absorptive dielectrics have been considered by the Jena group in a number of papers. Originally a Green's function method was employed [12,18], but in subsequent work a Hamiltonian formalism, involving some form of the Hamiltonian, (3.4), was used to study various physical situations [2,3,19]. Other recent contributions can be found in Refs. [17,20,21]. Longitudinal couplings play an essential role in Ref. [3], where intermolecular energy transfer is considered. However, use is made of a dipole approximation, which makes a comparison with the present approach not possible, since the unitary transformation breaks down. The same observation applies to other work, such as the microscopic approach by Juzeliūnas and Andrews [20], which also makes use of the dipole approximation, as is the case in Ref. [17]. Thus it seems unlikely that a Hamiltonian featuring V_{stat} can be retrieved from these approaches, once the dipole approximation has been made.

APPENDIX A: THE ATOMIC DECAY CONSTANTS

Here we give a short description of the use of the Feshbach projection technique to determine the poles in the lower complex half plane $\mathbb{C}^-$ of the analytic continuation of the object

$$([z-H]^{-1}\psi, \psi) = \langle \psi | [z-H]^{-1} | \psi \rangle, \quad \text{Im } z > 0, \qquad (A1)$$

in Eq. (2.7). If P is a projector, H an operator, and $Q = 1 - P$ then the Feshbach formula gives

$$P[z-H]^{-1}P = \{z - PHP - PHQ[z-QHQ]^{-1}QHP\}^{-1}P$$
$$= [z - H_{\text{eff}}(z)]^{-1}P. \qquad (A2)$$

Possible poles of this quantity are then given by the solutions of the equation

$$zP_0 = H_{\text{eff}}(z)P_0, \qquad (A3)$$

where P_0 is a projector with $P_0 \subseteq P$. In case P is finite-dimensional this is a relation for matrix-valued objects. In the case at hand we can take

$$P = |\psi\rangle\langle\psi| = |\varphi_2\rangle\langle\varphi_2| \otimes |\varphi_{\text{vac}}\rangle\langle\varphi_{\text{vac}}|, \tag{A4}$$

which is one-dimensional in which case $P_0 = P$ and Eq. (A3) is a scalar equation. However, if ψ is degenerate or if there are atomic states with energy close to λ_2 then P must be enlarged to take these states into account [5]. In order to keep the bookkeeping simple we shall assume that such states are either not present or can be neglected. As a consequence Eq. (A3) takes the form

$$z = H_{\text{eff}}(z). \tag{A5}$$

Now, neglecting quadratic terms in A, we have

$$H = H_f + H_{\text{at}} + \kappa H_{\text{int}}, \tag{A6}$$

where κ is a parameter that allows us to keep track of powers of the interaction in the sequel and

$$H_{\text{at}} = \frac{\mathbf{p}^2}{2m} + V_{\text{stat}},$$

$$H_{\text{int}} = \frac{e}{2m}\{\mathbf{p} \cdot A(\mathbf{x}) + A(\mathbf{x}) \cdot \mathbf{p}\}. \tag{A7}$$

Since $\langle\varphi_{\text{vac}}|A(\mathbf{x})|\varphi_{\text{vac}}\rangle = 0$ we have $PHQ = PH_{\text{int}}Q$. We shall also assume that atomic states different from φ_1 and φ_2 can be neglected in H_{at}. As a result we obtain

$$H_{\text{eff}}(z) = \lambda_2 + \kappa^2 \langle\varphi_2 \otimes \varphi_{\text{vac}}|H_{\text{int}}[z - QH_fQ - \lambda_1|\varphi_1\rangle\langle\varphi_1|$$
$$- \kappa QH_{\text{int}}Q]^{-1}H_{\text{int}}|\varphi_2 \otimes \varphi_{\text{vac}}\rangle. \tag{A8}$$

We can now expand $z = z(\kappa)$ in powers of κ, $z(\kappa) = z_0 + \kappa z_1 + \kappa^2 z_2 + \ldots$ [in more general situations $P_0 = P_0(\kappa)$ must also be expanded]. Then $z_0 = \lambda_2 + i0$, $z_1 = 0$, and

$$z_2 = \langle\varphi_2 \otimes \varphi_{\text{vac}}|H_{\text{int}}|\varphi_1\rangle[z_0 - \lambda_1 - H_f]^{-1}\langle\varphi_1|H_{\text{int}}|\varphi_2 \otimes \varphi_{\text{vac}}\rangle. \tag{A9}$$

Here we skipped the Q's around H_f since $H_{\text{int}}|\varphi_{\text{vac}}\rangle$ is already in the Q subspace. We now evaluate the various terms in this expression. Thus

$$\langle\varphi_1|H_{\text{int}}|\varphi_2 \otimes \varphi_{\text{vac}}\rangle = \frac{e}{2m}\sum_\beta \int d\mu\langle\varphi_1|(2\mu)^{-1/2}a^*(\mathbf{u}_{\mu\beta})$$
$$\times \{\mathbf{p} \cdot \overline{\mathbf{u}_{\mu\beta1}(\mathbf{x})} + \overline{\mathbf{u}_{\mu\beta1}(\mathbf{x})} \cdot \mathbf{p}\}|\varphi_2 \otimes \varphi_{\text{vac}}\rangle$$
$$= \frac{e}{2m}\sum_\beta \int d\mu(2\mu)^{-1/2}|\mathbf{u}_{\mu\beta}\rangle\langle\varphi_1|$$
$$\times \{\mathbf{p} \cdot \overline{\mathbf{u}_{\mu\beta1}(\mathbf{x})} + \overline{\mathbf{u}_{\mu\beta1}(\mathbf{x})} \cdot \mathbf{p}\}|\varphi_2\rangle, \tag{A10}$$

where

$$\langle\varphi_1|\{\mathbf{p} \cdot \overline{\mathbf{u}_{\mu\beta1}(\mathbf{x})} + \overline{\mathbf{u}_{\mu\beta1}(\mathbf{x})} \cdot \mathbf{p}\}|\varphi_2\rangle$$

$$= -i\int d\mathbf{x}[\overline{\varphi_1(\mathbf{x})}\partial_{\mathbf{x}} \cdot \{\overline{\mathbf{u}_{\mu\beta1}(\mathbf{x})}\varphi_2(\mathbf{x})\}$$
$$+ \overline{\varphi_1(\mathbf{x})}\mathbf{u}_{\mu\beta1}(\mathbf{x}) \cdot \partial_{\mathbf{x}}\varphi_2(\mathbf{x})]$$

$$= i\int d\mathbf{x}\overline{\mathbf{u}_{\mu\beta1}(\mathbf{x})} \cdot [\{\partial_{\mathbf{x}}\overline{\varphi_1(\mathbf{x})}\}\varphi_2(\mathbf{x}) - \overline{\varphi_1(\mathbf{x})}\partial_{\mathbf{x}}\varphi_2(\mathbf{x})]$$

$$= i\int d\mathbf{x}\overline{\mathbf{u}_{\mu\beta1}(\mathbf{x})} \cdot \mathbf{g}(\mathbf{x}), \tag{A11}$$

so

$$\langle\varphi_1|H_{\text{int}}|\varphi_2 \otimes \varphi_{\text{vac}}\rangle = i\frac{e}{2m}\sum_\beta \int d\mu(2\mu)^{-1/2}|\mathbf{u}_{\mu\beta}\rangle$$
$$\times \int d\mathbf{x}\overline{\mathbf{u}_{\mu\beta1}(\mathbf{x})} \cdot \mathbf{g}(\mathbf{x}) \tag{A12}$$

and similarly

$$\langle\varphi_2 \otimes \varphi_{\text{vac}}|H_{\text{int}}|\varphi_1\rangle = -i\frac{e}{2m}\sum_\beta \int d\mu(2\mu)^{-1/2}\langle\mathbf{u}_{\mu\beta}|$$
$$\times \int d\mathbf{x}\overline{\mathbf{g}(\mathbf{x})} \cdot \mathbf{u}_{\mu\beta1}(\mathbf{x}). \tag{A13}$$

Here we note that the atomic eigenfunctions not only depend on the relative electronic coordinate $\mathbf{r} = \mathbf{x} - \mathbf{X}$ but also on $\mathbf{X}$ since this is the case for V_{stat}. Thus $\mathbf{g} = \mathbf{g}(\mathbf{x}, \mathbf{X})$ or $\mathbf{g} = \mathbf{g}(\mathbf{r}, \mathbf{X})$. Since $H_f = \mu|\mathbf{u}_{\mu\beta}\rangle$ and $\langle\mathbf{u}_{\mu'\beta'}|\mathbf{u}_{\mu\beta}\rangle = \delta(\mu - \mu')\delta_{\beta\beta'}$ we end up with

$$\langle\varphi_2 \otimes \varphi_{\text{vac}}|H_{\text{int}}|\varphi_1\rangle[z_0 - \lambda_1 - H_f]^{-1}\langle\varphi_1|H_{\text{int}}|\varphi_2 \otimes \varphi_{\text{vac}}\rangle$$

$$= \left(\frac{e}{2m}\right)^2 \int d\mathbf{x}d\mathbf{y}\overline{\mathbf{g}(\mathbf{x})} \cdot \sum_\beta \int d\mu\langle\mathbf{x}|\mathbf{u}_{\mu\beta1}\rangle(2\mu)^{-1}$$

$$\times [\omega_0 + i0 - \mu]^{-1}\langle\mathbf{u}_{\mu\beta1}|\mathbf{y}\rangle \cdot \mathbf{g}(\mathbf{y}), \tag{A14}$$

where $\omega_0 = \lambda_2 - \lambda_1$ is the atomic transition frequency. Then, to leading order,

$$\text{Im } z = -\left(\frac{e}{2m}\right)^2 \int d\mathbf{x}d\mathbf{y}\overline{\mathbf{g}(\mathbf{x})} \cdot \sum_\beta \int d\mu\langle\mathbf{x}|\mathbf{u}_{\mu\beta1}\rangle$$

$$\times (2\mu)^{-1}\pi\delta(\omega_0 - \mu)\langle\mathbf{u}_{\mu\beta1}|\mathbf{y}\rangle \cdot \mathbf{g}(\mathbf{y})$$

$$= -\pi\left(\frac{e}{2m}\right)^2 \int d\mathbf{x}d\mathbf{y}\overline{\mathbf{g}(\mathbf{x})} \cdot \sum_\beta \int d\mu\langle\mathbf{x}|\mathbf{u}_{\mu\beta1}\rangle$$

$$\times \delta(\omega_0^2 - \mu^2)\langle\mathbf{u}_{\mu\beta1}|\mathbf{y}\rangle \cdot \mathbf{g}(\mathbf{y})$$

$$= -\frac{i}{2}\left(\frac{e}{2m}\right)^2 \int d\mathbf{x}d\mathbf{y}\overline{\mathbf{g}(\mathbf{x})} \cdot \langle\mathbf{x}|\mathsf{R}_e(\omega_0)$$

$$- \mathsf{R}_e(\omega_0)^*|\mathbf{y}\rangle \cdot \mathbf{g}(\mathbf{y}). \tag{A15}$$

The last step follows from

$$\sum_\beta \int d\mu|\mathbf{u}_{\mu\beta1}\rangle\delta(\omega_0^2 - \mu^2)\langle\mathbf{u}_{\mu\beta1}|$$

$$= \frac{1}{2\pi i}\sum_\beta \int d\mu|\mathbf{u}_{\mu\beta1}\rangle\{[\omega_0^2 - i0 - \mu^2]^{-1}$$

$$- [\omega_0^2 + i0 - \mu^2]^{-1}\}\langle\mathbf{u}_{\mu\beta1}|$$

$$= \frac{1}{2\pi i}\sum_\beta \int d\mu(|\mathbf{u}_{\mu\beta}\rangle\{[\omega_0^2 - i0 - \mu^2]^{-1}$$

$$- [\omega_0^2 + i0 - \mu^2]^{-1}\}\langle\mathbf{u}_{\mu\beta}|)_{11}$$

$$= \frac{1}{2\pi i}([\omega_0^2 - i0 - \mathsf{H}_e]^{-1} - [\omega_0^2 + i0 - \mathsf{H}_e]^{-1})_{11}$$

$$= \frac{1}{2\pi i}\{\mathsf{R}_e(\omega_0)^* - \mathsf{R}_e(\omega_0)\}. \tag{A16}$$

APPENDIX B: AN APPROXIMATE EXPRESSION FOR $\gamma_2^\perp$

As a first step we need to calculate the function

$$\mathbf{h}(\mathbf{r}) = \langle \mathbf{r}|[z^2 - \mathbf{p}^2]^{-1}\mathbf{g}^\perp\rangle, \quad z^2 = \omega_0^2 + i0, \tag{B1}$$

for the case that φ_1 and φ_2 are hydrogenic $1s$ and $2p$ states. Thus

$$\varphi_1(\mathbf{r}) = n_1 \exp[-\alpha r], \quad n_1 = \sqrt{\frac{\alpha^3}{\pi}},$$

$$\varphi_2(\mathbf{r}) = n_2 \mathbf{c} \cdot \mathbf{r} \exp[-\beta r], \quad n_2 = \sqrt{\frac{\beta^5}{\pi}}, \tag{B2}$$

where $\mathbf{c}$ is a real unit vector. In case they are eigenfunctions of the Coulomb Hamiltonian

$$H = \frac{1}{2m}\mathbf{p}^2 - \frac{e}{r}, \tag{B3}$$

with eigenvalues λ_1 and λ_2,

$$\beta = \frac{\alpha}{2}, \quad \alpha = me^2, \quad n = n_1 n_2,$$

$$\lambda_1 = \frac{me^4}{2}, \quad \lambda_2 = \frac{me^4}{8}. \tag{B4}$$

Then

$$\mathbf{g}(\mathbf{r}) = n\left\{\mu \mathbf{c} \cdot \mathbf{rr}\frac{1}{r} - \mathbf{c}\right\}\exp[-\nu r],$$

$$\mu = \beta - \alpha, \quad \nu = \beta + \alpha. \tag{B5}$$

Its Fourier transform is

$$\widetilde{\mathbf{g}}(\mathbf{k}) = (2\pi)^{-3/2}\int d\mathbf{r}\,\exp[i\mathbf{k}\cdot\mathbf{r}]\mathbf{g}(\mathbf{r})$$

$$= -n(2\pi)^{-3/2}4\pi\{\mu\mathbf{c}\cdot\partial_\mathbf{k}\partial_\mathbf{k} - \mathbf{c}\partial_\nu\}[\nu^2 + k^2]^{-1} \tag{B6}$$

and

$$\widetilde{\mathbf{g}}^\perp(\mathbf{k}) = (\mathsf{U} - \mathbf{e_k}\mathbf{e_k})\cdot\widetilde{\mathbf{g}}(\mathbf{k}). \tag{B7}$$

However, with $f = f(k, \nu) = [\nu^2 + k^2]^{-1}$,

$$\partial_\mathbf{k}\partial_\mathbf{k}f = \mathsf{U}\frac{1}{k}\partial_k f + \mathbf{e_k}\mathbf{e_k}k\partial_k\frac{1}{k}\partial_k f, \tag{B8}$$

so

$$(\mathsf{U} - \mathbf{e_k}\mathbf{e_k})\cdot\partial_\mathbf{k}\partial_\mathbf{k}f = (\mathsf{U} - \mathbf{e_k}\mathbf{e_k})\frac{1}{k}\partial_k f = (\mathsf{U} - \mathbf{e_k}\mathbf{e_k})\frac{1}{\nu}\partial_\nu f, \tag{B9}$$

resulting in

$$\widetilde{\mathbf{g}}^\perp(\mathbf{k}) = n(2\pi)^{-3/2}4\pi\left(1 - \frac{\mu}{\nu}\right)\partial_\nu\mathbf{c}\cdot(\mathsf{U} - \mathbf{e_k}\mathbf{e_k})[k^2 + \nu^2]^{-1}, \tag{B10}$$

and

$$\widetilde{\mathbf{h}}(\mathbf{k}) = -n(2\pi)^{-3/2}4\pi\left(1 - \frac{\mu}{\nu}\right)\partial_\nu$$

$$\times \mathbf{c}\cdot(\mathsf{U} - \mathbf{e_k}\mathbf{e_k})[k^2 - z^2]^{-1}[k^2 + \nu^2]^{-1}. \tag{B11}$$

Hence

$$\mathbf{h}(\mathbf{r}) = (2\pi)^{-3/2}\int d\mathbf{k}\,\exp[-i\mathbf{k}\cdot\mathbf{r}]\widetilde{\mathbf{h}}(\mathbf{k})$$

$$= -n(2\pi)^{-3}4\pi\left(1 - \frac{\mu}{\nu}\right)\partial_\nu[z^2 + \nu^2]^{-1}\mathbf{c}\cdot\int d\mathbf{k}$$

$$\times\exp[-i\mathbf{k}\cdot\mathbf{r}]\times(\mathsf{U} - \mathbf{e_k}\mathbf{e_k})\{[k^2 - z^2]^{-1}$$

$$- [k^2 + \nu^2]^{-1}\}$$

$$= \mathbf{h}_1(\mathbf{r}) + \mathbf{h}_2(\mathbf{r}). \tag{B12}$$

Recalling that $\mathbf{e_k} = k^{-1}\mathbf{k}$, $\mathbf{h}(\mathbf{r})$ can now be obtained using contour integral techniques. In $\mathbf{h}_1(\mathbf{r})$ the residue in $k = z$ is picked up and the result is a polynomial in r^{-1} times $\exp[i\omega_0 r]$, whereas for $\mathbf{h}_2(\mathbf{r})$ the residue in $k = i\nu$ is taken, resulting in $\mathbf{h}_2(\mathbf{r}) \sim \exp[-\nu r]$, which has exponential decay on an atomic scale. More precisely

$$\mathbf{h}_1(\mathbf{r}) = \rho\mathbf{c}\cdot\left(\mathsf{U} + \frac{1}{\omega_0^2}\partial_\mathbf{r}\partial_\mathbf{r}\right)\frac{\exp[i\omega_0 r]}{r},$$

$$\rho = 2n\frac{\nu - \mu}{(\omega_0^2 + \nu^2)^2}, \tag{B13}$$

and

$$\mathbf{h}_1(\mathbf{r})\cdot\overline{\mathbf{h}_1(\mathbf{r})} = \rho^2\{1 - (\mathbf{c}\cdot\mathbf{e_r})^2\}\frac{1}{r^2} + \mathcal{O}\left(\frac{1}{r^4}\right). \tag{B14}$$

For a dielectric filling a sphere with radius d, centered in the origin,

$$\mathrm{Im}\,\chi(\mathbf{x}, \omega_0) = \mathrm{Im}\,\chi(\omega_0)\theta(d - x),$$

$$\mathbf{x} = \mathbf{X} + \mathbf{r}, \tag{B15}$$

the corresponding contribution $\gamma_{2a}^\perp$ to $\gamma_2^\perp$ becomes

$$\gamma_{2a}^\perp = \frac{1}{2}\left(\frac{e\omega_0}{2m}\right)^2\mathrm{Im}\,\chi(\omega_0)\int d\mathbf{r}\,\theta(d - x)\mathbf{h}_1(\mathbf{r})\cdot\overline{\mathbf{h}_1(\mathbf{r})}. \tag{B16}$$

It is readily checked that $\theta(d-x)$ vanishes in a neighborhood of $\mathbf{r}=0$ for $X>d$, so the singularities of $\mathbf{h}_1(\mathbf{r})\cdot\overline{\mathbf{h}_1(\mathbf{r})}$ in $\mathbf{r}=0$

cause no problems. Switching to $\mathbf{x} = \mathbf{r} + \mathbf{X}$ and setting $\mathbf{X} = \kappa^{-1}\mathbf{e}$ then gives

$$\gamma_{2a}^{\perp} = \frac{1}{2}\left(\frac{e\omega_0}{2m}\right)^2 \mathrm{Im}\,\chi(\omega_0)$$

$$\times \int d\mathbf{x}\,\theta(d-x)\mathbf{h}_1(\mathbf{x}-\kappa^{-1}\mathbf{e}) \cdot \overline{\mathbf{h}_1(\mathbf{x}-\kappa^{-1}\mathbf{e})}.$$

(B17)

Expansion around $\kappa=0$ then gives (V is the volume of the sphere)

$$\gamma_{2a}^{\perp} = \frac{1}{2}\left(\frac{e\omega_0}{2m}\right)^2 \mathrm{Im}\,\chi(\omega_0)V\mathbf{c}\cdot(\mathsf{U}-\mathbf{ee})\mathbf{c}\kappa^2 + \mathcal{O}(\kappa^4)$$

$$= \frac{1}{2}\left(\frac{e\omega_0}{2m}\right)^2 \mathrm{Im}\,\chi(\omega_0)V\mathbf{c}\cdot(\mathsf{U}-\mathbf{ee})\cdot\mathbf{c}\frac{1}{X^2} + \mathcal{O}\left(\frac{1}{X^4}\right).$$

(B18)

In the corresponding longitudinal case we have, assuming $X>d$ and omitting technical details

$$\gamma^{\|} = \left(\frac{e}{2m\omega_0}\right)^2 \frac{\mathrm{Im}\,\chi(\omega_0)}{|1+\chi(\omega_0)|^2}(\theta(d-x)\mathbf{g}^{\|},\mathbf{g}^{\|})$$

$$= \left(\frac{e}{2m\omega_0}\right)^2 \frac{\mathrm{Im}\,\chi(\omega_0)}{|1+\chi(\omega_0)|^2}\int d\mathbf{r}\,\theta(d^2-|\mathbf{X}+\mathbf{r}|^2)|\mathbf{g}^{\|}(\mathbf{r})|^2$$

$$= \left(\frac{e}{2m\omega_0}\right)^2 \frac{\mathrm{Im}\,\chi(\omega_0)}{|1+\chi(\omega_0)|^2}\int_0^{\infty} dr\,r^2\int_0^{\pi} d\vartheta\,\sin\vartheta$$

$$\times \int_0^{2\pi} d\psi \times \theta(d^2-X^2-r^2-2r\cos\vartheta)|\mathbf{g}^{\|}(r,\vartheta,\psi)|^2.$$

(B19)

Performing the ψ integral and setting $\cos\vartheta=u$,

$$\gamma^{\|} = \left(\frac{e}{2m\omega_0}\right)^2 \frac{\mathrm{Im}\,\chi(\omega_0)}{|1+\chi(\omega_0)|^2}$$

$$\times \int_0^{\infty} dr\,r^2\int_{-1}^{+1} du\,\theta(d^2-X^2-r^2-2ru)m(r,u)$$

$$= \left(\frac{e}{2m\omega_0}\right)^2 \frac{\mathrm{Im}\,\chi(\omega_0)}{|1+\chi(\omega_0)|^2}\int_{X-d}^{X+d} dr\,n(X,r).$$

(B20)

Here $n(X,r)$ still contains $\exp[-2\nu r]$ so $\gamma^{\|}$ decays as $\exp[-2\nu X]$.

APPENDIX C: THE UNITARY TRANSFORMATION

We recast (ρ,φ) such that it features the electric field, which has advantages in the subsequent calculations. Thus

$$(\rho,\varphi) = -(\mathbf{W},\mathbf{E}) = -(\mathbf{W},\mathbf{E}^{\|}), \qquad (C1)$$

where the last equality follows from $\mathbf{W}$ being a gradient. Equation (C1) is readily verified by integrating by parts and using

$$\partial_{\mathbf{x}} \cdot \mathbf{W}(\mathbf{x}) = \partial_{\mathbf{x}}^2\sum_n \frac{e_n}{4\pi|\mathbf{x}-\mathbf{x}_n|} = -\sum_n e_n\delta(\mathbf{x}-\mathbf{x}_n) = -\rho(\mathbf{x}).$$

(C2)

Although (ρ,φ) does not vanish outside the absorptive medium, $\mathbf{E}^{\|}(\mathbf{x})$ does. This follows from Eq. (3.2) for $\mathbf{E}$ and the Helmholtz equation

$$[\omega^2\varepsilon(\mathbf{x},\omega) - \mathsf{h}] \cdot \mathsf{G}(\mathbf{x},\mathbf{y},\omega) = -\delta(\mathbf{x}-\mathbf{y})\mathsf{U}, \qquad (C3)$$

by writing

$$\varepsilon(\mathbf{x},\omega)\mathbf{E}(\mathbf{x},\omega) = \frac{i}{\sqrt{\pi}}[\omega^2\varepsilon(\mathbf{x},\omega) - \mathsf{h} + \mathsf{h}]$$

$$\times \int d\mathbf{y}\,\mathsf{G}(\mathbf{x},\mathbf{y},\omega) \cdot \sqrt{\mathrm{Im}\,\varepsilon(\mathbf{y},\omega)}\mathbf{f}(\mathbf{y},\omega)$$

$$= -\frac{i}{\sqrt{\pi}}\sqrt{\mathrm{Im}\,\varepsilon(\mathbf{x},\omega)}\mathbf{f}(\mathbf{x},\omega)$$

$$+ \frac{i}{\sqrt{\pi}}\mathsf{h} \cdot \int d\mathbf{y}\,\mathsf{G}(\mathbf{x},\mathbf{y},\omega) \cdot \sqrt{\mathrm{Im}\,\varepsilon(\mathbf{y},\omega)}\mathbf{f}(\mathbf{y},\omega),$$

(C4)

and noting that outside the medium $\varepsilon(\mathbf{x},\omega)=1$ and $\sqrt{\mathrm{Im}\,\varepsilon(\mathbf{x},\omega)}=0$, so $\mathbf{E}(\mathbf{x},\omega)$ is transverse outside.

We now calculate the transformed momenta and field variables. To start with the momenta

$$\mathbf{p}_n' = U\mathbf{p}_nU^{-1} = \mathbf{p}_n + i[(A^{\|},\mathbf{W}),\mathbf{p}_n] + \ldots = \mathbf{p}_n + i[(A^{\|},\mathbf{W}),\mathbf{p}_n],$$

(C5)

since the higher order commutators vanish. Here

$$i[(A^{\|},\mathbf{W}),\mathbf{p}_n] = -\partial_{\mathbf{x}_n}(A^{\|},\mathbf{W})$$

$$= \int d\mathbf{x}A^{\|}(\mathbf{x}) \cdot \partial_{\mathbf{x}}\partial_{\mathbf{x}}\frac{e_n}{4\pi|\mathbf{x}-\mathbf{x}_n|}$$

$$= \int d\mathbf{x}A^{\|}(\mathbf{x}) \cdot [-\mathsf{U}\partial_{\mathbf{x}}^2 + \partial_{\mathbf{x}}\partial_{\mathbf{x}} + \mathsf{U}\partial_{\mathbf{x}}^2]\frac{e_n}{4\pi|\mathbf{x}-\mathbf{x}_n|}$$

$$= \int d\mathbf{x}A^{\|}(\mathbf{x})\partial_{\mathbf{x}}^2\frac{e_n}{4\pi|\mathbf{x}-\mathbf{x}_n|}$$

$$= -e_n\int d\mathbf{x}A^{\|}(\mathbf{x})\delta(\mathbf{x}-\mathbf{x}_n) = -e_nA^{\|}(\mathbf{x}_n), \quad (C6)$$

so

$$\mathbf{p}_n' = \mathbf{p}_n - e_nA^{\|}(\mathbf{x}_n). \qquad (C7)$$

Here we used the fact that $\mathsf{U}\partial_{\mathbf{x}}^2-\partial_{\mathbf{x}}\partial_{\mathbf{x}}$ is proportional to the projector upon the transverse fields. We now turn to the field operators (again the higher order commutators vanish)

$$\mathbf{f}^*(\mathbf{x},\omega)' = (U\mathbf{f}^*U^{-1})(\mathbf{x},\omega) = \mathbf{f}^*(\mathbf{x},\omega) + \mathbf{g}^*(\mathbf{x},\omega), \quad (C8)$$

where

$$\mathbf{g}^*(\mathbf{x},\omega) = i[(A,\mathbf{W}),\mathbf{f}^*(\mathbf{x},\omega)]$$

$$= \frac{i\omega}{\sqrt{\pi}} \int d\mathbf{y}\mathbf{W}(\mathbf{y}) \cdot \mathsf{G}(\mathbf{y},\mathbf{x},\omega+i0)\sqrt{\mathrm{Im}\,\varepsilon(\mathbf{x},\omega)}. \tag{C9}$$

Taking adjoints

$$\mathbf{f}'(\mathbf{x},\omega) = \mathbf{f}(\mathbf{x},\omega) + \mathbf{g}(\mathbf{x},\omega),$$

$$\mathbf{g}(\mathbf{x},\omega) = -\frac{i\omega}{\sqrt{\pi}}\sqrt{\mathrm{Im}\,\varepsilon(\mathbf{x},\omega)} \int d\mathbf{y}\mathsf{G}(\mathbf{x},\mathbf{y},\omega-i0) \cdot \mathbf{W}(\mathbf{y}). \tag{C10}$$

Thus, for the field Hamiltonian

$$H'_f = \int d\mathbf{x}\int_0^\infty d\omega\omega\{\mathbf{f}^*(\mathbf{x},\omega) + \mathbf{g}^*(\mathbf{x},\omega)\} \times \{\mathbf{f}(\mathbf{x},\omega) + \mathbf{g}(\mathbf{x},\omega)\}$$

$$= H_f + \int d\mathbf{x}\int_0^\infty d\omega\omega\{\mathbf{f}^*(\mathbf{x},\omega) \cdot \mathbf{g}(\mathbf{x},\omega) + \mathbf{g}^*(\mathbf{x},\omega) \cdot \mathbf{f}(\mathbf{x},\omega)\}$$

$$+ \int d\mathbf{x}\int_0^\infty d\omega\omega\mathbf{g}^*(\mathbf{x},\omega) \cdot \mathbf{g}(\mathbf{x},\omega). \tag{C11}$$

For the second term we obtain

$$\int d\mathbf{x}\int_0^\infty d\omega\omega\{\mathbf{f}^*(\mathbf{x},\omega) \cdot \mathbf{g}(\mathbf{x},\omega) + \mathbf{g}^*(\mathbf{x},\omega) \cdot \mathbf{f}(\mathbf{x},\omega)\}$$

$$= \int d\mathbf{x}\mathbf{W}(\mathbf{x}) \cdot E^{\parallel}(\mathbf{x}) = \int d\mathbf{x}\mathbf{W}(\mathbf{x}) \cdot E(\mathbf{x}) = (\mathbf{W},E). \tag{C12}$$

The last term is more difficult to calculate

$$\int d\mathbf{x}\int_0^\infty d\omega\omega\mathbf{g}^*(\mathbf{x},\omega) \cdot \mathbf{g}(\mathbf{x},\omega)$$

$$= \frac{1}{\pi}\int d\mathbf{y}d\mathbf{u}d\mathbf{x}\mathbf{W}(\mathbf{y}) \cdot \int_0^\infty d\omega\omega^3,$$

$$\mathsf{G}(\mathbf{y},\mathbf{x},\omega+i0) \cdot \mathrm{Im}\,\varepsilon(\mathbf{x},\omega)\mathsf{G}(\mathbf{x},\mathbf{u},\omega-i0) \cdot \mathbf{W}(\mathbf{u})$$

$$= \frac{1}{\pi}\int d\mathbf{y}d\mathbf{u}\mathbf{W}(\mathbf{y}) \cdot \int_0^\infty d\omega\omega^3$$

$$\times \langle\mathbf{y}|\mathsf{R}_e(\omega+i0) \cdot \mathrm{Im}\,\varepsilon(\mathbf{x},\omega)\mathsf{R}_e^*(\omega+i0)|\mathbf{u}\rangle \cdot \mathbf{W}(\mathbf{u}). \tag{C13}$$

But $\mathsf{R}_e(z)$ satisfies the resolvent identity

$$\mathsf{R}_e(z) \cdot \mathrm{Im}\,\varepsilon(\mathbf{x},z)\mathsf{R}_e^*(z) = \frac{i}{2\omega^2}\{\mathsf{R}_e(z) - \mathsf{R}_e^*(z)\}, \tag{C14}$$

so

$$\frac{1}{\pi}\int_0^\infty d\omega\omega^3\langle\mathbf{y}|\mathsf{R}_e(\omega+i0) \cdot \mathrm{Im}\,\varepsilon(\mathbf{x},\omega)\mathsf{R}_e^*(\omega+i0)|\mathbf{u}\rangle$$

$$= -\frac{1}{2\pi i}\int_0^\infty d\omega\omega\{\langle\mathbf{y}|\mathsf{R}_e(\omega+i0)|\mathbf{u}\rangle - \langle\mathbf{y}|\mathsf{R}_e^*(\omega+i0)|\mathbf{u}\rangle\}$$

$$= -\frac{1}{2\pi i}\int_0^\infty d\omega\omega\{\langle\mathbf{y}|\mathsf{R}_e(\omega+i0)|\mathbf{u}\rangle - \mathsf{R}_e(-\omega+i0)|\mathbf{u}\rangle\}$$

$$= -\frac{1}{2\pi i}\int_{-\infty}^\infty d\omega\omega\langle\mathbf{y}|\mathsf{R}_e(\omega+i0)|\mathbf{u}\rangle. \tag{C15}$$

Next we note that $\mathsf{R}_e(z)$ is the $1-1$ component of $[z^2 - \mathsf{H}_e]^{-1}$ in the auxiliary field formalism and

$$\frac{1}{2\pi i}\int_\Gamma dz z[z^2 - \mathsf{H}_e]^{-1} = -\frac{1}{2}\mathsf{Q}_e, \tag{C16}$$

where $\mathsf{Q}_e = 1 - \mathsf{P}_e$ with P_e the projector upon the null space of H_e, and $\Gamma = \mathbb{R} + i\delta$, $\delta > 0$. Thus

$$\frac{1}{\pi}\int_0^\infty d\omega\omega^3\langle\mathbf{y}|\mathsf{R}_e(\omega+i0) \cdot \mathrm{Im}\,\varepsilon(\mathbf{x},\omega)\mathsf{R}_e^*(\omega+i0)|\mathbf{u}\rangle$$

$$= \frac{1}{2}\langle\mathbf{y}|\mathsf{Q}_{e11}|\mathbf{u}\rangle = \frac{1}{2}\delta(\mathbf{y}-\mathbf{u}) - \frac{1}{2}\langle\mathbf{y}|\mathsf{P}_{e11}|\mathbf{u}\rangle, \tag{C17}$$

so

$$\int d\mathbf{x}\int_0^\infty d\omega\omega\mathbf{g}^*(\mathbf{x},\omega) \cdot \mathbf{g}(\mathbf{x},\omega)$$

$$= \frac{1}{2}\int d\mathbf{y}\mathbf{W}(\mathbf{y})^2 - \frac{1}{2}\int d\mathbf{y}d\mathbf{u}\mathbf{W}(\mathbf{y}) \cdot \langle\mathbf{y}|\mathsf{P}_{e11}|\mathbf{u}\rangle \cdot \mathbf{W}(\mathbf{u})$$

$$= \frac{1}{2}\int d\mathbf{y}\mathbf{W}(\mathbf{y})^2 - \frac{1}{2}(\mathsf{P}_{e11} \cdot \mathbf{W},\mathbf{W}). \tag{C18}$$

Dismissing self-energies

$$\frac{1}{2}\int d\mathbf{y}\mathbf{W}(\mathbf{y})^2 = \frac{1}{2}\int d\mathbf{y}\{-\partial_\mathbf{y}\zeta_0(\mathbf{y})\} \cdot \{-\partial_\mathbf{y}\zeta_0(\mathbf{y})\}$$

$$= -\frac{1}{2}\int d\mathbf{y}\zeta_0(\mathbf{y})\partial_\mathbf{y}^2\zeta_0(\mathbf{y})$$

$$= \frac{1}{2}\int d\mathbf{y}\zeta_0(\mathbf{y})\rho(\mathbf{y})$$

$$= V_{\mathrm{Coul}}. \tag{C19}$$

For the remaining term we need P_{e11}, which is, according to Ref. [1], Eq. (2.17),

$$\mathsf{P}_{e11} = \mathbf{p}[\mathbf{p} \cdot \varepsilon_{\mathrm{stat}}(\mathbf{x})\mathbf{p}]^{-1}\mathbf{p}, \tag{C20}$$

so

$$\frac{1}{2}(\mathsf{P}_{e11} \cdot \mathbf{W}, \mathbf{W}) = \frac{1}{2}(\mathbf{p}[\mathbf{p} \cdot \varepsilon_{\text{stat}}(\mathbf{x})\mathbf{p}]^{-1}\mathbf{p} \cdot \mathbf{W}, \mathbf{W})$$

$$= \frac{1}{2}([\mathbf{p} \cdot \varepsilon_{\text{stat}}(\mathbf{x})\mathbf{p}]^{-1}\mathbf{p} \cdot \mathbf{W}, \mathbf{p} \cdot \mathbf{W})$$

$$= \frac{1}{2}([\mathbf{p} \cdot \varepsilon_{\text{stat}}(\mathbf{x})\mathbf{p}]^{-1}\partial_{\mathbf{x}} \cdot \mathbf{W}, \partial_{\mathbf{x}} \cdot \mathbf{W})$$

$$= \frac{1}{2}([\mathbf{p} \cdot \varepsilon_{\text{stat}}(\mathbf{x})\mathbf{p}]^{-1}\rho, \rho) = V_{\text{stat}}, \quad (C21)$$

where again self-interactions are discarded. Thus

$$\int d\mathbf{x} \int_0^\infty d\omega \omega \mathbf{g}^*(\mathbf{x}, \omega) \cdot \mathbf{g}(\mathbf{x}, \omega) = V_{\text{Coul}} - V_{\text{stat}}. \quad (C22)$$

Note that, since we are dealing with the difference $V_{\text{Coul}} - V_{\text{stat}}$ and both have the same self-interactions, the latter do not occur if we regroup the various terms in a suitable way. Finally,

$$(\rho, \varphi)' = -(\mathbf{W}, \mathbf{E})' = -(\mathbf{W}, \mathbf{E}) - i[(\mathbf{A}, \mathbf{W}), (\mathbf{W}, \mathbf{E})]. \quad (C23)$$

Using similar techniques as before, this becomes

$$(\rho, \varphi)' = -(\mathbf{W}, \mathbf{E}) - 2\{V_{\text{Coul}} - V_{\text{stat}}\}. \quad (C24)$$

Collecting results we arrive at

$$H' = H_f + \sum_n \frac{1}{2m_n}[\mathbf{p}_n - e_n \mathbf{A}(\mathbf{x}_n)]^2 + V_{\text{stat}}. \quad (C25)$$

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