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Quantum frequency shifts near a plasma surface

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Abstract. The electromagnetic field coupled to a model of a semi-infinite plasma is quantized. A technical difficulty, related to the choice of gauge in the presence of the plasma surface, is resolved by appeal to the Power–Zienau transformation, far enough to allow level shifts to be calculated for nearby overall-neutral atoms or molecules outside the plasma. Charged systems are not covered. The level shifts, functions of plasma frequency and distance, are displayed as Laplace transforms, simple asymptotic forms being given for small and for large distances. Special treatment is needed for excited states. The results are compared to a recently proposed classical model; and to expressions based on Lifshitz's theory, which appears to be neither designed nor adequate to deal with excited states.

1. Introduction

If an excited atom radiates not in isolation but near a macroscopic body, then both the emission rate and the frequency of the light suffer changes that depend on the distance between the body and the atom. Quantum mechanics gives the rate by the golden rule, and the frequency shift as the difference between the energy shifts of the initial and final levels. But recently, Chance *et al* (1974, 1975a,b,c; these authors will be referred to as CPS) have given classical arguments which provide some interesting insight; they also have the advantage that they deal directly with the frequency shift, and can easily accommodate realistic optical properties of the macroscopic medium. By contrast, beginning with Lifshitz (1955) (see also Dzyaloshinskii *et al* 1961), very powerful quantum methods have been developed for evaluating the ground state shift; the recent literature can be traced from Heinrichs (1975) and Mukhopadhyay and Lundqvist (1975). This method can also accomodate quite involved properties of the medium; but in its present state of development it is not applicable to excited states (nor consequently to frequency shifts). One can discover this limitation either from the details of the theory, or more quickly by noting that by design it is essentially an equilibrium theory, which is of course compatible with its successes when applied to molecular forces.

Thus the situation is ripe for beginning to construct a full quantum treatment of such effects against which other approaches can be assessed; and in the present exploratory attack on frequency shifts it seemed safest to set up a simple model of the medium which can be dealt with explicitly and transparently by elementary perturbation theory. Such explicit treatment lessens the risk, which experience in this field shows to be serious, that complicated or very general formalism used *ab initio* may obscure, or even mask a mishandling of, the basic physics. It also brings into the open a problem in quantizing the electromagnetic field in the presence of an interface which as far as we know has not been stated before. We feel that it would be unwise to expect such a problem to be dissolved, behind the scene as it were, by some general response-function type formalism, rather than resolve it explicitly. In this context it is also unwise to trust the popular oversimplified atomic models, because the harmonic oscillator model has peculiarities making it deceptive in assessing the limits of validity of classical analogies, while the two-level model is inconsistent with quantum mechanics, as was shown elsewhere (Barton 1974, to be referred to as I). Indeed, the relation between classical and quantum results will turn out more subtle than might perhaps have been expected, and does not admit of classical prediction of frequency shifts (though it is useful for widths); while for excited states the results of the Lifshitz theory, naively applied, are sometimes right and sometimes wrong.

The simplest situation is one where the medium, taken to occupy the half-space $z < 0$, is a perfect conductor, excluding electromagnetic fields completely. The atom is placed *in vacuo* a distance z outside the medium. The frequency shifts for this case were given in I; and the linewidth has been discussed by Philpott (1973). In the present paper we make the minimal extension needed to illustrate the effects of field penetration into real media. To this end we construct a model inspired by some of the relevant features of a metallic plasma; qualitatively speaking we retain its collective but not its single-particle aspects. The medium is defined to consist of a continuous charged fluid, having mass density Mn, charge density en, plus an immobile, uniform, overall-neutralizing background distribution of density $-en_0$, with n_0 the equilibrium value of n. The equations for the medium are linearized in the displacement $\xi(\boldsymbol{r}, t)$ from equilibrium; hydrodynamic pressure and the static distortion of n near the surface are neglected. Accordingly we have $n = n_0 - n_0 \operatorname{div} \xi$, and there are volume charge and current densities given by

$$\rho = -en_0 \operatorname{div} \xi, \qquad j = en_0 \dot{\xi} \tag{1.1}$$

and a surface charge density on the interface (the $z = 0$ plane) given by

$$\sigma = en_0 \xi_\perp (z = 0^-). \tag{1.2}$$

(Subscripts $\perp$ and $\parallel$ denote components of vectors normal and parallel to the interface.) In linearized approximation there are no genuine surface currents, since these would be proportional to $\sigma\dot{\xi}$, which by (1.2) is quadratic in ξ.

The model thus defined is widely used as the starting point for discussing surface problems; for instance by Elson and Ritchie (1971, to be referred to as ER). As for its resemblance to real metals, the neglect of pressure effects and of equilibrium surface distortion is probably acceptable at least qualitatively, provided the atomic distance z is well above the Fermi wavelength and the Thomas–Fermi screening length. More serious may be the failure of the model to accomodate Ohm's law at low frequencies. But such dissipative effects could be allowed for, from first principles, only by introducing statistical mechanics as well as quantum mechanics, and we want to avoid this in order to retain as clear a view as possible of the consequences of the latter alone. (By contrast, one could fairly easily introduce natural vibrations of the medium governed by mechanical, ie not explicitly by electromagnetic, restoring forces, making a model of an insulator rather than of a metal.) The reason why our model has been so drastically simplified is that no further non-trivial approximations are then needed to deal with the quantum mechanics of its coupling to the Maxwell field, and that one can exhibit in reasonably simple form the final expression for the level shifts, and especially its asymptotics for small and for large values of z. For further discussions of the limits of applicability of the model, see Heinrichs (1975) and Mukhopadhyay and Lundqvist (1975).

The decay rate in this model has already been calculated in an exemplary paper by Philpott (1975); hence we shall concentrate exclusively on the energy shifts. In § 2.1 we outline the quantization of the medium coupled to the Maxwell field, proceeding through the classical normal modes, essentially in the footsteps of ER. Here one meets the difficulty mentioned earlier, which is closely related to the choice of gauge and to the coupling between field and atom. Luckily, for neutral systems, it can be sidestepped by aid of the Power-Zienau transformation. These problems are discussed and resolved in outline in § 2.2, which can be skipped by readers already convinced by § 2.1. The treatment of charged systems is reserved for another paper. In § 3 we outline the ordinary second-order perturbation calculation of the ground state shift, and rewrite the result as a Laplace transform for later convenience. In § 4 we simplify the ground state expression in some interesting special cases, and in the asymptotic regions where $z \to 0$ or $z \to \infty$. In § 5 we deal with the shifts of excited states; these are relatively easy to handle given the results of §§ 3 and 4, though no provision is made for them by the Lifshitz formalism in its present state, which is precisely one of the motivations of this paper. It turns out, *a posteriori*, that for small z, corrections peculiar to excited states are unimportant, and that the Lifshitz theory naively applied gives correct results; but that they dominate for large z where they completely swamp the famous Casimir–Polder potential and where they, alone, are responsible for any 'correspondence' between classical and quantum results. In § 6 we summarize our results and compare them with earlier approximate or classical ones.

2. Normal-mode expansion and field quantization

In § 2.1 we quantize the Maxwell field and the semi-infinite medium in mutual interaction, employing the standard elementary procedure which identifies the normal modes, expands the fields in terms of these, and imposes commutation rules turning the expansion coefficients into annihilation and creation operators. This method is adopted in order to postpone for as long as possible the problems which in a canonical field theory procedure force one either to introduce an indefinite metric or, adopting Coulomb gauge, to treat formally unretarded electrostatic forces on a different footing from all other effects (Bjorken and Drell 1965); both procedures being particularly unsuited to a semi-infinite medium. It turns out that the elementary method suffices if the atomic or molecular system (henceforth 'atom' for short) whose energy shift we need is overall neutral; then the interaction Hamiltonian between it and the Maxwell field is $-\boldsymbol{d} \cdot \boldsymbol{E}$, where $\boldsymbol{d}$ is the atomic electric dipole moment operator and $\boldsymbol{E}$ the electric field. The problems uncovered by any attempt to deal simultaneously with charged systems and with retardation are discussed in § 2.2, together with the outline justification of § 2.1 in terms of the standard canonical Coulomb-gauge quantization and its interaction Hamiltonian (which is equation (2.22) below).

2.1. *Elementary quantization*

In its essentials we follow the method of ER, and refer to them for details; but must extend it to (partially) transmitted waves with frequencies $\omega > \omega_p$, where ω_p is the plasma frequency given by

$$\omega_p^2 = 4\pi e^2 n_0 / M. \tag{2.1}$$

We use natural units, $\hbar = 1 = c$, with $e^2/\hbar c \simeq 1/137$. The equations of motion are Newton's law for the medium (neglecting the Lorentz force), and Maxwell's equations for the field. Their linearized form, for harmonic normal modes with time dependence $e^{-i\omega t}$, is

$$-\omega^2 M\boldsymbol{\xi} = e\boldsymbol{E} \tag{2.2}$$

which allows $\boldsymbol{\xi}$ to be eliminated in favour of $\boldsymbol{E}$, and

$$\begin{aligned} \operatorname{div}\boldsymbol{E} &= -4\pi n_0 e \operatorname{div}\boldsymbol{\xi}, \qquad \operatorname{div}\boldsymbol{B} = 0 \\ \operatorname{curl}\boldsymbol{E} &= \mathrm{i}\omega\boldsymbol{B} \\ \operatorname{curl}\boldsymbol{B} &= -\mathrm{i}\omega\boldsymbol{E} - \mathrm{i}\omega 4\pi e n_0 \boldsymbol{\xi}. \end{aligned} \tag{2.3}$$

Whenever n_0 or ω_p appear in a field equation or a volume integral, it is understood that they behave as if they had as a factor the step function $\theta(-z)$, (not shown), ie they have constant values for $z < 0$ and vanish for $z > 0$. The effective boundary conditions at the interface follow from Maxwell's equations themselves: $\boldsymbol{B}$ and $\boldsymbol{E}_{\parallel}$ are continuous, and

$$E_{\perp}(z = 0+) - E_{\perp}(z = 0-) = 4\pi\sigma = 4\pi e n_0 \xi_{\perp}(z = 0-) \tag{2.4}$$

where (1.2) has been used in the last step. The total energy of medium plus Maxwell field (not a Hamiltonian at this stage!), is

$$\mathscr{E} = \int \mathrm{d}V \left(\frac{1}{2} n_0 M \dot{\boldsymbol{\xi}}^2 + \frac{1}{8\pi}(\boldsymbol{E}^2 + \boldsymbol{B}^2) \right). \tag{2.5}$$

Equations (2.2)–(2.4) admit two types of normal modes. The longitudinal modes have $\boldsymbol{B} = 0$ everywhere, $\boldsymbol{E} = 0$ for $z > 0$, and $\operatorname{curl}\boldsymbol{E} = 0$, $\operatorname{div}\boldsymbol{E} \neq 0$ for $z < 0$. It is well known, and § 2.2 will confirm it, that these modes are not coupled to any neutral system wholly outside the medium; hence we ignore them from now on. The other, so called transverse, modes have $\operatorname{div}\boldsymbol{E} = 0$ for $z > 0$ and $z < 0$, ie everywhere except on the interface, where $\operatorname{div}\boldsymbol{E}$ has a $\delta(z)$-type singularity. Hence it is convenient to introduce a vector potential $\boldsymbol{A}$:

$$\boldsymbol{B} = \operatorname{curl}\boldsymbol{A}, \qquad \boldsymbol{E} = -\dot{\boldsymbol{A}} \tag{2.6}$$

and to choose a gauge so that

$$\operatorname{div}\boldsymbol{A} = 0 \qquad \text{for } z \neq 0. \tag{2.7}$$

As discussed in § 2.2, this is *not* the usual Coulomb or radiation gauge; but with it we shall need no scalar potential, in the sense that the normal mode amplitudes, the energy $\mathscr{E}$, and later on the atomic coupling, are expressible in terms of $\boldsymbol{A}$ alone.

The so called transverse modes subdivide into three-dimensional modes (photons) and surface plasmons. The photon modes are expressible in the form

$$\boldsymbol{A}(\boldsymbol{\rho}, z) = N \exp(-\mathrm{i}\omega t + \mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\rho})\boldsymbol{f}(q, z) \tag{2.8}$$

where the N are norming constants to be chosen later, $\boldsymbol{k}$ and $\boldsymbol{\rho}$ are two-component vectors parallel to the interface, and q is the vacuum wavenumber normal to the interface. For photon modes,

$$\omega = (k^2 + q^2)^{1/2}. \tag{2.9}$$

In §§ 3, 4 and 5 we shall need ω for real k but complex q. In the complex q plane, ω is defined by branch cuts along the imaginary axis from $\mathrm{i}k$ to $\mathrm{i}\infty$ and from $-\mathrm{i}k$ to $-\mathrm{i}\infty$; ω

is real positive along the real q axis and along the uncut part of the imaginary axis, and positive (negative) imaginary on the right (left) edge of the upper cut. We shall also need a function Q of q alone,

$$Q = (q^2-\omega_p^2)^{1/2} \tag{2.10}$$

having a cut from $q = -\omega_p$ to $q = +\omega_p$ along the real axis, real positive (negative) for $q > \omega_p (q < -\omega_p)$, and having positive imaginary part when $\mathrm{Im}\, q > 0$. Throughout this paper, when q is real and on this cut, it shall be understood to be on the upper edge of the cut, where Q is positive imaginary. Finally, it is convenient to define $\epsilon(\omega)$, which in the classical theory plays the role of dielectric function,

$$\epsilon(\omega) = 1-\omega_p^2/\omega^2. \tag{2.11}$$

At this point one is in a position to determine the normal modes by explicit calculation. We confine ourselves to displaying the results for only those parts of $\boldsymbol{A}$ which describe (partially) transmitted waves, having therefore $q > \omega_p$, and denoted by $\boldsymbol{A}_>$; and to adapating from ER the part describing surface plasmons, denoted by $\boldsymbol{A}_{sp}$. For the totally reflected waves $\boldsymbol{A}_<$ having $q < \omega_p$ we refer to ER; note that for each value of $\boldsymbol{k}$ and q, and for each polarization s or p, there are two independent modes in $\boldsymbol{A}_>$, but only one in $\boldsymbol{A}_<$. The fields displayed will suffice to illustrate all the results needed later. In the following formulae, $\hat{\boldsymbol{z}}$ and $\hat{\boldsymbol{k}}$ are unit vectors in the indicated directions, and HC stands for 'Hermitean conjugate'.

s-polarized photons with $q > \omega_p$

$$\boldsymbol{A}_{s,>} = \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}\boldsymbol{k} \int_{\omega_p}^{\infty} \mathrm{d}q\, \mathrm{e}^{\mathrm{i}\boldsymbol{k}.\boldsymbol{\rho}}\hat{\boldsymbol{k}}\times\hat{\boldsymbol{z}}\left[\left(\frac{4}{\omega(1+Q/q)}\right)^{1/2}(\theta(-z)\cos Qz+\theta(z)\cos qz)a_{s1}(\boldsymbol{k},q) + \left(\frac{4}{\omega(1+q/Q)}\right)^{1/2}\left(\theta(-z)\frac{q}{Q}\sin Qz+\theta(z)\sin qz\right)a_{s2}(\boldsymbol{k},q)\right]+\mathrm{HC}. \tag{2.12}$$

p-polarized photons with $q > \omega_p$

$$\boldsymbol{A}_{p,>} = \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}\boldsymbol{k} \int_{\omega_p}^{\infty} \mathrm{d}q\, \mathrm{e}^{\mathrm{i}\boldsymbol{k}.\boldsymbol{\rho}}\left\{\left(\frac{4k^2}{\omega^3(1+Q/\epsilon q)}\right)^{1/2}\left[\theta(-z)\frac{1}{\epsilon}\left(\hat{\boldsymbol{z}}\cos Qz-\mathrm{i}\hat{\boldsymbol{k}}\frac{Q}{k}\sin Qz\right) + \theta(z)\left(\hat{\boldsymbol{z}}\cos qz-\mathrm{i}\hat{\boldsymbol{k}}\frac{q}{k}\sin qz\right)\right]a_{p1}(\boldsymbol{k},q)+\left(\frac{4k^2q^2}{\omega^3(1+\epsilon q/Q)}\right)^{1/2} \times\left[\theta(-z)\left(\hat{\boldsymbol{z}}\frac{1}{Q}\sin Qz+\mathrm{i}\hat{\boldsymbol{k}}\frac{1}{k}\cos Qz\right)+\theta(z)\left(\hat{\boldsymbol{z}}\frac{1}{q}\sin qz+\mathrm{i}\hat{\boldsymbol{k}}\frac{1}{k}\cos qz\right)\right] \times a_{p2}(\boldsymbol{k},q)\right\}+\mathrm{HC}. \tag{2.13}$$

Surface plasmons. These amplitudes decay exponentially with increasing $|z|$, and are fully specified by the momentum $\boldsymbol{k}$ alone. Their frequencies $\tilde{\omega}$ are given by

$$\tilde{\omega}^2 = \tfrac{1}{2}\omega_p^2+k^2-(\tfrac{1}{4}\omega_p^4+k^4)^{1/2} \tag{2.14}$$

ranging from 0 for $k^2 = 0$ to $\frac{1}{2}\omega_p^2$ as $k^2 \to \infty$. Define quantities $\tilde{q}$ and $\tilde{Q}$, related to $\boldsymbol{k}$ and $\tilde{\omega}$ in the same way as q/i and Q/i relate to $\boldsymbol{k}$ and ω:

$$\tilde{q}^2 = k^2-\tilde{\omega}^2, \qquad \tilde{Q}^2 = k^2-\tilde{\omega}^2+\omega_p^2. \tag{2.15}$$

Define also

$$\tilde{\epsilon} = \epsilon(\tilde{\omega})$$

and the norming function

$$p(k) = \frac{\tilde{\epsilon}^4 - 1}{\tilde{\epsilon}^2(|\tilde{\epsilon} + 1|)^{1/2}}. \tag{2.16}$$

Then ER's expression for A_{sp} becomes (bearing in mind that their medium occupies the half space $z > 0$)

$$A_{sp} = \frac{1}{2\pi}\int_{-\infty}^{\infty} dk\, e^{ik.\rho}\left(\frac{4\pi}{p(k)}\right)^{1/2}\left[\theta(-z)\left(i\hat{k} + \hat{z}\frac{k}{\tilde{Q}}\right)e^{\tilde{Q}z}\right.$$
$$\left. + \theta(z)\left(i\hat{k} - \hat{z}\frac{k}{\tilde{q}}\right)e^{-\tilde{q}z}\right]a(k) + \text{HC}. \tag{2.17}$$

The commutation rules are that each a and a^+ operator in equations (2.12), (2.13) and (2.17) commutes with all others except its own Hermitean conjugate: eg

$$[a_{s1}(k, q), a_{s1}^+(k', q')] = \delta(k - k')\delta(q - q'). \tag{2.18}$$

Normalizations have been so chosen that, on adjoining ER's expression for $A_<$, and substituting $A = (A_> + A_< + A_{sp})$ into (2.5) via (2.6) and (2.7), one obtains the Hamiltonian operator (dropping the zero-point energy),

$$H = \int_{-\infty}^{\infty} dk \int_0^{\infty} dq\, \omega\left(\theta(\omega_p - q)(a_s^+ a_s + a_p^+ a_p) + \theta(q - \omega_p)\sum_{\lambda=1,2}(a_{s\lambda}^+ a_{s\lambda} + a_{p\lambda}^+ a_{p\lambda})\right)$$
$$+ \int_{-\infty}^{\infty} dk\, \tilde{\omega}(k) a^+(k) a(k) \tag{2.19}$$

where ω, a_s, a_p, $a_{s\lambda}$ and $a_{p\lambda}$ are functions of q and k.

The quantized fields are coupled to a neutral atomic system situated outside the medium by

$$H_{int} = -d \cdot E \tag{2.20}$$

where $E = -\dot{A}$ is the electric field at the system and d is the total electric dipole moment operator. The variation of E across the system, ie higher multipoles, will be ignored for simplicity. For a single-electron atom with fixed (infinitely massive) nucleus, to which we confine ourselves most of the time for definiteness, one has

$$H_{int} = -er \cdot E \tag{2.21}$$

where r is the position vector of the electron relative to the nucleus. The coupling (2.20) is justified in § 2.2.

2.2. *Coulomb gauge and Power–Zienau transformation*

The standard canonical way to quantize the Maxwell field (Bjorken and Drell 1965) is to express its transverse-electric and its magnetic components in terms of A, with $\text{div}\, A = 0$ everywhere (as in equation (2.6) but with E replaced by E_T alone), its longitudinal-electric part as $E_L = -\nabla\phi$, to quantize A, and to express ϕ in terms of the instantaneous charge density ρ through the unretarded Poisson equation $\nabla^2\phi = -4\pi\rho$. Particles of charge e and mass m are then coupled to the field not by (2.20), but by

$$H'_{\text{int}} = e\phi - eA \,.\, p/m + e^2A^2/2m. \tag{2.22}$$

In a truly infinite medium the argument of § 2.1 still proceeds straightforwardly, the A field introduced there being identified with that of the Coulomb gauge, and the coupling to particles other than those subsumed into the medium represented by (2.22). The only change needed is to drop the reflected components and the surface waves from A. (An elegant diagonalization of the field–medium coupling has been given by Chappell *et al* (1965); the canonical treatment of the analogous problem for an infinite insulator is due to Hopfield (1958, § 3). But for our semi-infinite medium the expressions of § 2.1 are not those applicable in the Coulomb gauge, because A (and E) have non-zero divergence on the interface (see equations (1.2) and (2.4)), and because we have not introduced the scalar potential which in Coulomb gauge is due to the surface charge (1.2).

At this stage it is not obvious how to proceed; certainly one must not use the expansion of A given in § 2.1 jointly with the coupling (2.22), because we have not yet produced a definition of ϕ compatible with that of A. Though it would be fairly straightforward to do this for a purely passive medium, it is not quite so easy for our case of an active medium not describable by a frequency-independent dielectric constant.

Luckily, in the case of a neutral atomic system wholly outside the medium, the dilemma just described can be sidestepped by appeal to the canonical transformation of Power and Zienau (Power and Zienau 1959, Power 1964, Woolley 1971), and we now outline the sequence of the argument. First, envisage the Hamiltonian for medium, atom, plus Maxwell field, with true Coulomb-gauge coupling of the type (2.22) of field to medium and field to atom. Then the Power–Zienau transformation essentially replaces all these couplings by new couplings of the $-\boldsymbol{d}\,.\,\boldsymbol{E}$ type between each matter system and the quantized field E, which is now required to be transverse (to have div $E = 0$) only outside the medium and the atom. In the transformed Hamiltonian, there is also a new term H_{self}, containing the effects of the longitudinal field internal to each matter system separately. Thus, the longitudinal plasma oscillations, just like the unperturbed atomic energy levels, appear as consequences precisely of H_{self}, which however contains no direct interaction between the matter systems, and is irrelevant to the interaction of each matter system with the quantized field.

In the final step one diagonalizes that part of the Hamiltonian which contains the transverse Maxwell field and the transverse oscillations of the medium, either implicitly, by finding the normal modes as in § 2.1, or formally by adapting the method of Chappell *et al* (1965) to a semi-infinite rather than an infinite medium. Then one arrives precisely at the prescription given in § 2.1.

Unfortunately, the Power–Zienau transformation is not applicable to systems with non-zero total charge. For instance, in order to calculate the interaction between the medium and an external electron, we should be forced back to the coupling (2.22) and should have to recast the treatment of the active medium so as to produce a consistent prescription for ϕ as well as for A. It is remarkable that the need for such a full treatment has not yet been felt in the literature on surface effects. This is due to a coincidence; those who, like ER, have taken full account of retardation, have not had to deal with charged particles; while those who have dealt with charged particles have neglected retardation. In this context, to neglect retardation means that one works from the outset in the limit $c \to \infty$, where there are only electrostatic forces and potentials governed by Poisson's equation, and that one finds and quantizes the normal modes of the medium directly in this theory. An elegant example of this procedure is the work of Brako *et al*

(1975). As far as we know, the published literature contains at most one clue (perhaps in the paper by Mahan 1972) that in quantum mechanics it may be awkward to treat charged systems and retardation together in surface problems.

Finally, one should perhaps underline the paradoxical status of surface plasmons in the $c \to \infty$ limit as compared with the real world. For $c \to \infty$, one has $\tilde{\omega} = \omega_p/\sqrt{2}$ for all wavelengths, short or long, and curl $\boldsymbol{E} = 0$ everywhere; by contrast, with c finite, $\tilde{\omega} = \omega_p/\sqrt{2}$ is achieved only for infinitely *short* wavelength, and the surface modes are unmistakably transverse, having curl $\boldsymbol{E} \neq 0$ everywhere.

3. Ground state shift

In this section we calculate the z-dependent part $\Delta(z)$ of the ground state energy shift by elementary perturbation theory. The z-independent part, which contains the ordinary Lamb shift and diverges, is dropped systematically, so that by definition $\Delta(\infty) = 0$. By this step one abandons the guaranteed negative-definite property of second-order ground state shifts. It will become obvious presently why excited states are reserved for separate treatment in § 5. For simplicity we deal explicitly with a single-electron atom; the results are easily adapted for arbitrary neutral molecular systems. In summations over atomic states $|j\rangle$, we encounter the energy difference $E_{j0} = E_j - E_0$, and matrix elements $|\langle j|r_i|0\rangle|^2$, where $|0\rangle$ is always the state whose shift Δ is being calculated. To ease the notation we shall often write these quantities as E and r_i^2, whenever the context prevents confusion. The summation index j will also be dropped from Σ_j. Note that the atom-to-medium distance z is not the third component of the internal atomic coordinate $\boldsymbol{r}$, and that $r_z^2 \equiv r_\perp^2$, $r_\parallel^2 \equiv r_x^2 + r_y^2$. We shall need the expressions for the static atomic polarizability, parallel and normal to the interface, of the state $|0\rangle$

$$\Pi_\parallel = e^2 \sum_j |\langle j|r_\parallel|0\rangle|^2/E_{j0} = e^2 \sum r_\parallel^2/E$$
$$\Pi_\perp = 2e^2 \sum r_\perp^2/E \tag{3.1}$$

and the oscillator sum rule for each Cartesian component r_i of $\boldsymbol{r}$:

$$\sum r_i^2 E = 1/2m. \tag{3.2}$$

For more complex systems, $e\boldsymbol{r}$ is replaced by the appropriate total electric dipole operator $\boldsymbol{d}$. For instance, consider a rigidly-rotating diatomic molecule with Hamiltonian $L^2/2I$, moment of inertia I, and suppose that the electronic dipole moments are neglected, so that $\boldsymbol{d} = (\delta e)\boldsymbol{R}$, where δe is a charge difference and $\boldsymbol{R}$ the relative position vector of the two nuclei. Then in (3.1) we simply replace $e\boldsymbol{r} \to \boldsymbol{d}$, while a simple calculation shows that (3.2) is replaced by

$$\sum_j |\langle j|d_i|0\rangle|^2 E_{j0} = \langle 0|(\boldsymbol{d}^2 - d_i^2)|0\rangle/2I \tag{3.3}$$

as a consequence of the commutator $\boldsymbol{L} \times \boldsymbol{d} = \mathrm{i}\boldsymbol{d}$.

The perturbation is H_{int} (equation (2.21)); the Hamiltonian for the field is (2.19). Let $|0, 0\rangle$ contain the atom in its ground state $|0\rangle$, and no quanta excited; and $|\gamma, j\rangle$ the atom in its state $|j\rangle$ and a quantum of type γ excited, where γ can be a surface plasmon or an s- or p-polarized photon with $q > \omega_p$ (suffix $>$) or $q < \omega_p$ (suffix $<$); and let ω_γ

be the energy of the quantum (ie $\omega_\gamma = \omega(\boldsymbol{k}, q)$ or $\omega = \tilde{\omega}(\boldsymbol{k})$). Then

$$\Delta = -\sum_\gamma \sum_j \frac{|\langle \gamma, j | H_{\text{int}} | 0, 0 \rangle|^2}{E_{j0} + \omega_\gamma}. \tag{3.4}$$

When $|0\rangle$ is the ground state, $E_{j0} > 0$ for all j and no denominators vanish.

We consider in turn the contribution from the various types of quanta.

From *s*-photons, with $q > \omega_\mathrm{p}$, we obtain straightforwardly, using (2.12),

$$\Delta_{\mathrm{s},>} = -\frac{e^2}{2\pi\omega_\mathrm{p}^2} \sum \int_0^\infty \mathrm{d}k\, k \int_{\omega_\mathrm{p}}^\infty \mathrm{d}q\, r_\parallel^2 \frac{\omega}{E+\omega} \cos(2qz)(q-Q)^2 \tag{3.5}$$

having already performed the integral over the direction of $\boldsymbol{k}$; the factor $\cos 2qz$ enters through the identity $\cos^2 qz = \frac{1}{2}(1+\cos 2qz)$ after dropping the z-independent part.

It turns out that the contribution from s-photons with $q < \omega_\mathrm{p}$ is also expressible in the form (3.5), if the q integration ranges from 0 to ω_p, and the real part of the result is taken (recall that Q is imaginary in this region, and the definitions in § 2.1). It is convenient to combine $\Delta_{\mathrm{s},>} + \Delta_{\mathrm{s},<} = \Delta_\mathrm{s}$ and to rewrite Δ_s so that the q integration extends along the entire real axis (above the cut due to Q). This gives

$$\Delta_\mathrm{s} = -\frac{e^2}{4\pi\omega_\mathrm{p}^2} \sum \int_0^\infty \mathrm{d}k\, k \int_{-\infty}^\infty \mathrm{d}q\, \mathrm{e}^{2\mathrm{i}qz}(q-Q)^2 \frac{\omega}{E+\omega} r_\parallel^2. \tag{3.6}$$

Finally, we recast Δ_s as a Laplace transform, by deforming the q integration path, for fixed k, so that it runs along the upper branch cut due to ω, from $\mathrm{i}\infty$ to $\mathrm{i}k$ on its left edge and from $\mathrm{i}k$ to $\mathrm{i}\infty$ on its right edge. Writing

$$q = \mathrm{i}y$$

this yields a double integral with limits $\int_0^\infty \mathrm{d}k \int_k^\infty \mathrm{d}y \ldots$, in which we interchange the order of integration to $\int_0^\infty \mathrm{d}y \int_0^y \mathrm{d}k \ldots$. The result is

$$\Delta_\mathrm{s} = -\frac{e^2}{2\pi\omega_\mathrm{p}^2} \sum E r_\parallel^2 \int_0^\infty \mathrm{d}y\, \mathrm{e}^{-2yz} (\sqrt{y^2+\omega_\mathrm{p}^2} - y)^2 \int_0^y \mathrm{d}k\, k \frac{\sqrt{y^2-k^2}}{E^2+y^2-k^2}. \tag{3.7}$$

The k integral is elementary and gives

$$\Delta_\mathrm{s} = -\frac{e^2}{2\pi\omega_\mathrm{p}^2} \sum E r_\parallel^2 \int_0^\infty \mathrm{d}y\, \mathrm{e}^{-2yz} (\sqrt{y^2+\omega_\mathrm{p}^2} - y)^2 \left(y - E \tan^{-1} \frac{y}{E} \right) \tag{3.8}$$

The principal branch of the arctangent is meant.

For p-photons, similar steps lead to the analogue of (3.6)

$$\Delta_\mathrm{p} = \frac{e^2}{4\pi\omega_\mathrm{p}^2} \sum \int_0^\infty \mathrm{d}k\, k \int_{-\infty}^\infty \mathrm{d}q\, \mathrm{e}^{2\mathrm{i}qz}(q-Q)^2 \frac{1}{\omega(E+\omega)} (q^2 r_\parallel^2 - 2k^2 r_\perp^2) \left(1 - \frac{2Qq}{\omega^2 - \alpha^2} \right) \tag{3.9}$$

where

$$\alpha^2(q) = q(q-Q) = q(q - \sqrt{q^2 - \omega_\mathrm{p}^2}). \tag{3.10}$$

When deforming the q integration contour, one must now be careful to pick up residues from the poles at $\omega^2 = \alpha^2$, which have no counterpart in Δ_s. Accordingly, we write

$$\Delta_\mathrm{p} = \Delta_\mathrm{p}(\text{cut}) + \Delta_\mathrm{p}(\text{pole}) \tag{3.11}$$

and find eventually the analogue of (3.8)

$$\Delta_p(\mathrm{cut}) = \frac{e^2}{2\pi\omega_p^2}\sum E\int_0^\infty \mathrm{d}y\, \mathrm{e}^{-2yz}(\sqrt{y^2+\omega_p^2}-y)^2\Big[(r_\parallel^2+2r_\perp^2)\frac{y^2}{E}\tan^{-1}\frac{y}{E}$$
$$-2y^2\sqrt{y^2+\omega_p^2}\,(yr_\parallel^2+2\sqrt{y^2+\omega_p^2}\,r_\perp^2)\frac{1}{E^2-\alpha^2}\left(\frac{1}{\alpha}\tan^{-1}\frac{y}{\alpha}-\frac{1}{E}\tan^{-1}\frac{y}{E}\right)$$
$$-2r_\perp^2\left(y-E\tan^{-1}\frac{y}{E}\right)+4y\sqrt{y^2+\omega_p^2}\,r_\perp^2\frac{1}{E}\tan^{-1}\frac{y}{E}\Big] \tag{3.12}$$

where, as in all subsequent equations

$$\alpha^2 \equiv \alpha^2(\mathrm{i}y) = y(\sqrt{y^2+\omega_p^2}-y). \tag{3.13}$$

Similarly one obtains

$$\Delta_p(\mathrm{pole}) = \frac{e^2}{2\omega_p^2}\sum\frac{1}{E}\int_0^\infty \mathrm{d}y\,\mathrm{e}^{-2yz}(\sqrt{y^2+\omega_p^2}-y)^2y^2\sqrt{y^2+\omega_p^2}$$
$$\times\frac{1}{\alpha(E+\alpha)}(yr_\parallel^2+2\sqrt{y^2+\omega_p^2}\,r_\perp^2). \tag{3.14}$$

Finally we need Δ_{sp}. From (2.17) one obtains directly

$$\Delta_{sp} = -e^2\sum\int_0^\infty \mathrm{d}k\,k\mathrm{e}^{-2\tilde{q}z}\frac{\tilde{\omega}^2}{p(k)(E+\tilde{\omega})}\left(r_\parallel^2+\frac{2k^2}{\tilde{q}^2}r_\perp^2\right). \tag{3.15}$$

Changing the integration variable from k to $\tilde{q}$, one discovers eventually that Δ_{sp} identically cancels Δ_p(pole) as given by (3.14). Hence the total shift is just $\Delta = \Delta_s + \Delta_p$(cut). Before combining them we can use the sum rule (3.2) to simplify those terms in the integrands which contain E only as a multiplicative factor, like the first term in the last bracket in (3.8). Then by adding (3.8) and (3.12) we obtain our final result for the ground state shift:

$$\Delta = \frac{e^2}{2\pi\omega_p^2}\int_0^\infty \mathrm{d}y\,\mathrm{e}^{-2yz}(\sqrt{y^2+\omega_p^2}-y)^2\Big\{-\frac{2y}{m}+\sum\Big[(r_\parallel^2+2r_\perp^2)(E^2+y^2)\tan^{-1}\frac{y}{E}$$
$$+r_\perp^2 4y\sqrt{y^2+\omega_p^2}\tan^{-1}\frac{y}{E}-2y^2\sqrt{y^2+\omega_p^2}\,(yr_\parallel^2+2\sqrt{y^2+\omega_p^2}\,r_\perp^2)$$
$$\times\frac{E}{E^2-\alpha^2}\left(\frac{1}{\alpha}\tan^{-1}\frac{y}{\alpha}-\frac{1}{E}\tan^{-1}\frac{y}{E}\right)\Big]\Big\}. \tag{3.16}$$

4. Ground state asymptotics and special cases

4.1. Special limits

Though the full expression (3.16) may look forbidding, it simplifies in many special but interesting limits. We shall consider: (i) the non-retarded (NR) limit $c \to \infty$; (ii) the 'perfect-conductor' (PC) limit $\omega_p \to \infty$ (so called because the medium then excludes the field completely), which was obtained in I; and, more interesting, the asymptotic expansions for small z and for large z in powers of z^{-1}. Not all these limits are interchangeable. Each term in Σ_j is effectively a function of two dimensionless variables, say zE_{j0} and $z\omega_p$, as well as of a dimensional variable (say e^2/z); thus the small-z asymptotics apply when one has both $z\omega_p \ll 1$ and $zE_{j0} \ll 1$ for the dominant terms in Σ_j, and similarly for the large-z region. Therefore the limit $\omega_p \to \infty$ is not compatible with $z \to 0$ asymptotics, whereas it is compatible with $z \to \infty$ asymptotics. Even for large ω_p, in the sense that $\omega_p \gg E_{j0}$ for all important states j, there is still a narrow region where $z\omega_p \leqslant 1$, and the perfect-conductor results apply only outside this region. These provisos must be borne in mind while interpreting the perfect-conductor and the asymptotic approximations.

To obtain the NR limit we restore factors of c in (3.18) by replacing $e^2 \to e^2/c$, $\omega_p^2 \to \omega_p^2/c^2$, $E \to E/c$, and multiplying overall by c^2 to get the right dimensions. One finds

$$\lim_{c\to\infty} \Delta \equiv \Delta_{\mathrm{NR}} = -\frac{e^2}{4}\sum \frac{\omega_p/\sqrt{2}}{E+\omega_p/\sqrt{2}}(r_\parallel^2 + 2r_\perp^2)\int_0^\infty \mathrm{d}y\, \mathrm{e}^{-2yz}y^2$$

$$\Delta_{\mathrm{NR}}(\omega_p, z) = -\frac{e^2}{16z^3}\sum \frac{\omega_p/\sqrt{2}}{E+\omega_p/\sqrt{2}}(r_\parallel^2 + 2r_\perp^2). \tag{4.1}$$

Though the limit $c \to \infty$ as such is academic, we shall see that the function Δ_{NR} enters also in other contexts.

The perfect-conductor limit of (3.18) is

$$\lim_{\omega_p\to\infty} \Delta \equiv \Delta_{\mathrm{PC}}(z) = \frac{e^2}{2\pi}\int_0^\infty \mathrm{d}y\, \mathrm{e}^{-2yz}\sum \tan^{-1}\frac{y}{E}[(E^2 - y^2)r_\parallel^2 - (E^2+y^2)2r_\perp^2] \tag{4.2}$$

which is equivalent to equations (2.14) and (2.16) in I (noting the identity $\tan^{-1}\lambda + \tan^{-1}1/\lambda = \pi/2$).

4.2. *Small distances*

This is the most promising region for experiment since Δ is largest here. For comparison, the perfect-conductor result ($\omega_p \to \infty$ first, $z \to 0$ second), obtained in I, is

$$\Delta_{\mathrm{PC}}(z) \sim \left(-\frac{e^2}{16z^3}\langle 0|(r_\parallel^2 + 2r_\perp^2)|0\rangle + \frac{e^2}{4\pi m z^2} + \frac{e^2}{8m^2 z}\langle 0|(p_\parallel^2 - 2p_\perp^2)|0\rangle + \mathrm{O}(\ln z)\right) \tag{4.3}$$

where $\boldsymbol{p}$ is the momentum conjugate to $\boldsymbol{r}$. The $\mathrm{O}(z^{-3})$ term is the Lennard-Jones (1932) potential, simply the expectation value of the electrostatic image energy due to the atomic dipole $e\boldsymbol{r}$. The other terms in (4.3) are commented on in I.

To obtain the $z \to 0$ asymptotic expansion of (3.16), we note that for $z \to 0$ the y integration diverges at its upper limit; hence we expand the integrand, apart from the factor e^{-2yz}, in ascending powers of y^{-1}, as for large y, and integrate term by term. For simplicity we consider only terms diverging like a power as $z \to 0$. As $y \to \infty$, y/α and y/E both diverge; note in particular the expansion

$$\tan^{-1}\frac{y}{E_{j0}} = \left(\frac{\pi}{2} - \frac{E_{j0}}{y} + \frac{1}{3}\frac{E_{j0}^3}{y^3} - \dots\right) - \pi\theta(-E_{j0}). \tag{4.4}$$

When (4.4) is substituted into (3.16), the last term, containing $\theta(-E_{j0})$, gives a contribution δ_j^*. If $|0\rangle$ is the ground state, every δ_j^* vanishes because every $E_{j0} > 0$, but δ^* survives for excited states and will be needed when discussing them in § 5.

The actual expansion beyond the leading term is tedious, and we quote only

$$\Delta(\omega_p, z) \sim \Delta_{\mathrm{NR}}(\omega_p, z) + \mathrm{O}(z^{-1}) \tag{4.5}$$

where Δ_{NR} is the same function which enters the $c \to \infty$ limit (4.1). The $\mathrm{O}(z^{-1})$ term is too cumbrous to be worth quoting. Comparing (4.5) with Δ_{PC} in (4.3) we see that as far as their respective leading terms are concerned, the order of the limits $\omega_p \to \infty$ and $z \to 0$ can be interchanged, though one has no right to expect this, as explained in §4.1. More remarkable is that Δ, in contrast to Δ_{PC}, lacks a term of $O(z^{-2})$. Though the $O(z^{-2})$ part of Δ_{PC} is common to all states and consequently cancels from frequency shifts, it would be observable in principle by measuring the force between atom and metal. The absence of such a component from the more realistic expression (4.5) suggests that with real metals the observed potential (Shih *et al* 1974, Shih 1974) should follow the z^{-3} law rather closely.

Though in most cases of interest one expects $\omega_p > E_{j0}$, it is amusing to consider the limit of Δ_{NR} for $\omega_p/E \ll 1$. By equation (3.1), this gives

$$\lim_{\omega_p \to 0} \Delta_{NR} \sim -(\omega_p/16z^3\sqrt{2})(\Pi_{\parallel}+\Pi_{\perp}). \tag{4.6}$$

4.3. *Large distances*

As $z \to \infty$, the integral in (3.16) is dominated by the region next to its lower limit; hence one expands the integrand in ascending powers of y, as for small y, and integrates term by term. In this case the expansion contains no terms, like δ^*, depending non-analytically on the sign of E. Irrespective of the value of ω_p, provided it is non-zero, one finds straightforwardly the same famous Casimir–Polder potential which applies for perfect conductors:

$$\Delta \sim -(2\Pi_{\parallel}+\Pi_{\perp})/8\pi z^4 + O(z^{-6}). \tag{4.7}$$

This is not surprising, because the physics of the Casimir–Polder argument implies that as $z \to \infty$, Δ should depend only on the static (zero-frequency) polarizability of the atom and of the metal; and at zero frequency there is perfect screening in our model even for finite ω_p. Alternatively, the fact that the leading term of Δ, as $z \to \infty$, is independent of ω_p, could have been foreseen from the dependence of Δ on the dimensionless variable $z\omega_p$. The apparent paradox that as $\omega_p \to 0$, the plasma vanishes, while the shift (4.7) does not, is resolved because (4.7) ceases to apply once $\omega_p z \leqslant 1$, and as $(\omega_p z) \to 0$ is replaced by (4.6) which does vanish with ω_p.

5. Excited states

Even when $|0\rangle$ is not the ground state, the expressions (3.6), (3.9) and (3.15) apply, provided we preface the integrals with the Cauchy principal-value prescription P when $E_j < E_0$, so that E_{j0} is negative and the denominators $(E+\omega_y)$ can vanish. Thus the technical problem is to modify the contour deformations which led from (3.6) and (3.9) to the final Laplace transforms, in order to take account of the vanishing denominators. For the frequency shift, $(\Delta_i - \Delta_f)$, of the atomic transition $i \to f$, this is an unavoidable complication, because in the sum giving Δ_i, the state f will certainly enter and introduce it. For a first-excited to ground-state transition this is the only dangerous term, but in general there may be several in both Δ_i and Δ_f.

The integrands of Δ_s and Δ_p now have poles in the q plane at $\omega = |E|$, which, depending on the ratio $k/|E|$, can lie either on the real axis or on the imaginary axis below the branch point at ik. In the former case the P integration path must be completed by small semicircles around these poles before it can be deformed, in the way discussed in

§3 and a correction term added to Δ in consequence. When the new poles are on the imaginary axis, we need only pick up their residues in addition to the contribution from the ik to i∞ cut, which gave Δ. Let us denote by Δ_j^* the new contribution to Δ from just one such state j having $E_j < E_0$, so that the total shift Δ_T becomes (suppressing the summation index j on Δ_j^*),

$$\Delta_T = \Delta + \sum_j \theta(-E_{j0})\Delta^*. \tag{5.1}$$

The evaluation of Δ_j^* is straightforward though it demands care; in particular there is once again a cancellation between contributions from p-photons and surface plasmons. Eventually, one finds, with $\alpha^2(\mathrm{i}y)$ as given in (3.13),

$$\Delta^* = \frac{e^2}{2\omega_p^2}\,\mathrm{Re}\int_C \mathrm{d}y\, \mathrm{e}^{-2yz}(\sqrt{y^2+\omega_p^2}-y)^2\Bigg[E^2 r_\parallel^2 + [2E^2 r_\perp^2 + y^2(r_\parallel^2 + 2r_\perp^2)]\left(1 + \mathrm{P}\frac{2y\sqrt{y^2+\omega_p^2}}{E^2-\alpha^2(\mathrm{i}y)}\right)\Bigg]. \tag{5.2}$$

The integration contour C runs along the imaginary y axis from $-\mathrm{i}|E|$ to 0, and then along the real axis to $+\infty$. The two portions of C arise from the two possible pole positions in the q plane, noted above. The principal value prescription is needed when $0 < E^2 < \omega^2/2$, for then the integrand has a pole on the positive real axis.

Note that no straightforward attempt to continue (3.16) analytically to negative E will yield the correct expression for excited state shifts; one must go back to (3.6), (3.9) and (3.15). Like the exact expression for Δ itself, (5.2) is rather uninformative at first sight, but simplifies in the two asymptotic regions.

Deal first with small distances. In addition to Δ^* we must include the correction δ^* defined just below equation (4.4). But $(\Delta^* + \delta^*)$ remains bounded as $z \to 0$. To see this, consider Δ^* as given in equation (5.2); for small z, only the large-y integration region is relevant. Hence, up to bounded terms, we can drop the part of the contour C between $-\mathrm{i}|E|$ and the origin, and need extend the y integral only from 0 to $+\infty$ along the real axis. But it is easy to verify that this integral is identically the negative of δ^*, obtainable from (3.16) by taking only the terms with factors $\tan^{-1}(y/E)$ and then replacing all these factors by $-\pi$. The conclusion is that, as $z \to 0$, the total shift is given even for excited states by the expansion (4.5), obtained in this limit from (3.16) and (4.4) while simply ignoring the last (θ function) term of (4.4). This prescription is correct up to terms remaining finite as $z \to 0$.

It follows in particular that $\Delta_{NR}(\omega_p, z)$, as given in (4.1), remains the leading term even for excited states. If the sum contains a term with $E_{j0} \simeq -\omega_p/\sqrt{2}$, then there will be a strong enhancement of Δ. In the strict non-retarded limit this is understood as a near-resonance (degeneracy), between the atom and the surface plasmons, which in that limit all share the unique frequency $\omega_p/\sqrt{2}$. For finite c it is due to the discontinuity in the density of states where the surface plasmon spectrum cuts off at $\omega_p/\sqrt{2}$.

By contrast, at large distances there are drastic changes peculiar to excited states. Since now there are no corrections to the asymptotic form of Δ itself, already calculated, equation (4.7) (see the remark at the start of § 4.3), one need only add to Δ the large-z asymptotic form of Δ^* in equation (5.2), obtainable by the method explained in § 4.3. Note first that the integration path C can be completed by a small detour round the pole on the real axis (when, for $0 < E^2 < \omega_p^2/2$, such a pole is present), since the correction for this introduces only terms vanishing exponentially with increasing z, and hence negligible in comparison with the inverse-power terms we already have. After completing the contour, it may be deformed, away from the origin, to run from $-\mathrm{i}|E|$ to ∞ along any convenient path in the right-half plane. This reduces the problem to finding the asymptotic expansion of the function

$$g(z) \equiv \int_{-\mathrm{i}|E|}^{\infty} \mathrm{d}y\, \mathrm{e}^{-2yz} f(y) \tag{5.3}$$

where

$$\Delta^* = (e^2/2\omega_p^2)\,\mathrm{Re}\, g, \tag{5.4}$$

$f(y)$ being defined by comparing (5.2), (5.3) and (5.4). But a standard piece of mathematics leads to the asymptotic series

$$g(z) \sim \frac{\mathrm{e}^{2\mathrm{i}|E|z}}{2z} \sum_{n=0}^{\infty} (2z)^{-n} f^{(n)}(-\mathrm{i}|E|) \tag{5.5}$$

where $f^{(n)}(y) \equiv \mathrm{d}^n f/\mathrm{d}y^n$.

It is convenient to define, for each E_{j0}, a dimensionless variable $x_j \equiv x \equiv 2|E_{j0}|z$. Then, one finds

$$\Delta^* \sim e^2|E|^3\, \mathrm{Re}\, \mathrm{e}^{\mathrm{i}x}\left[\frac{(\sqrt{\omega_p^2 - E^2} + \mathrm{i}|E|)^2}{\omega_p^2}\right] \times\left\{ r_{\|}^2\left(\frac{1}{x} + \frac{\mathrm{i}}{x^2}\right) + r_{\perp}^2 \frac{2\mathrm{i}}{x^2}\right\} + \mathrm{O}(x^{-3}). \tag{5.6}$$

The $\mathrm{O}(x^{-3})$ terms are too cumbersome to be worth quoting. Evidently, as $z \to \infty$, Δ^* with its terms of order z^{-1} and z^{-2} completely dominates Δ, which decreases like z^{-4}. In the limit $\omega_p \to \infty$, (5.2) and (5.6) correctly reduce to the corresponding perfect-conductor results in I.

The factor in square brackets in (5.6) is the classical Fresnel reflection coefficient F of the medium for light of frequency $|E|$ incident normally:

$$F = (\epsilon^{1/2} - 1)/(\epsilon^{1/2} + 1), \qquad \epsilon = 1 - \omega_p^2/E^2. \tag{5.7}$$

Some insight into why F should enter here is obtainable from the classical model of CPS (1974, 1975, a,b). They consider a classical dipole oscillating with frequency $|E_{j0}|$ in front of a mirror, under a given mechanical restoring force, and calculate the change in frequency due to the action on the dipole of its own retarded field reflected from the mirror. We refer to them for the full classical arguments and make only the following observation. It is to be expected that the $\mathrm{O}(z^{-1})$ component of the field should be reflected from the mirror to the dipole with the same reflection coefficient F which applies for light, since both are purely transverse waves. When the details are followed through, this accounts, at least by analogy, for the term $r_{\|}^2/x$ in (5.6) That F should be so directly relevant to both $\mathrm{O}(x^{-2})$ terms as well is an unexpected bonus.

6. Conclusions and comparisons

We summarize our main findings and compare them briefly to classical analogues and to earlier results. Such comparisons were motivated in the introduction.

The simple model of a plasma defined in § 1 was quantized in § 2.1, adequately to calculate the effects on a nearby neutral molecular system. The method was justified in §22, in which we also pointed out the problems in extending it to charged systems. The exact energy shift Δ of the neutral system ground state is (3.16). Its asymptotic form for small distances z is indicated in (4.5), the dominant term Δ_{NR} (equation (4.1)) coinciding with the limit of Δ as $c \to \infty$. The asymptotic form for large z is (4.7), the Casimir–Polder potential. For excited states the full level shift is $(\Delta + \Sigma_j \Delta_j^*)$, containing the addend $\Sigma_j \Delta_j^*$ given in (5.2), where one Δ_j^* enters for each level j below the one whose shift is in question. For small z, the asymptotic expansion of $(\Delta + \Sigma_j \Delta_j^*)$ has the same analytic form, namely (4.5), as for the ground state; in other words for small z no special attention need be paid to excited states as such in the end result, though this emerges only *a posteriori*. But for large z, the Δ_j^* dominate, and are given asymptotically in (5.6).

We mentioned an analogy, relevant at large z, between individual terms Δ_j^* in the *level* shift, and the *frequency* shift of a classical oscillator with frequency $|E_{j0}|$. This analogy is inspired by the recent work on classical models by CPS (1974, 1975 a, b). Though it allows some insight, it is ineffective for prediction except for first-excited to ground-state transitions observed at large z, for reasons given in the first paragraph of §5; and it depends on envisaging a correspondence between *transition matrix elements* and the classical oscillating dipole amplitude.

At small z, and in the special case of a 'perfect conductor' (infinite plasma frequency ω_p), there is a very different type of correspondence, namely, between the *expectation value* of the squared dipole operator and the square of the classical dipole moment. This appears in the Lennard-Jones potential, the leading term of (4.3). But in the more general expression $\Delta_{NR}(\omega_p, z)$, equation (4.1), valid for finite ω_p, this correspondence is largely lost or at least obscured, because the result once again depends on sums of squared transition matrix elements. Some classical analogies could be salvaged even from this expression by representing the atom as a collection of oscillators, but to modern eyes the details would not be illuminating.

To avoid all ambiguity we should state that we believe CPS (1975c) to be mistaken when they ascribe to Barton (1974) the conclusion that classical shifts dominate at all distances. Possibly this misunderstanding arises from applying the general formulae given in I for a perfect conductor to the very special case of a harmonic oscillator 'atom', and taking at face value some coincidences in the frequency shifts (even though the coincidences do not occur in the level shifts themselves). In any case we believe that the classical theory has no predictive power as regards frequency shifts, though, as demonstrated by CPS taken together with Philpott's (1975) work, it is valuable as regards widths.

More important is to compare our results with those first derived from Lifshitz' theory by Mavroyannis (1963), whose work is still the most accessible exposition. Note that Mavroyannis gives only averages over atomic orientations; hence we must replace $r_\parallel^2 \to \frac{2}{3}r^2$, $r_\perp^2 \to \frac{1}{3}r^2$ before comparing our results with his, and we understand that this has been done.

Mavroyannis has two expressions, one stated to be exact but too difficult to evaluate, and the other, his equation (16), approximate but stated to be correct for small z. Our comments apply mainly to the latter. After some integrations by parts it can be expressed in our notation as

$$\Delta_M = -\frac{2e^2}{3\pi}\sum Er^2 \frac{\omega_p^2/2}{E^2-\omega_p^2/2}\int_0^\infty dy\, e^{-2yz}y^2\left(\frac{1}{\omega_p/2^{1/2}}\tan^{-1}\frac{y}{\omega_p/2^{1/2}}-\frac{1}{E}\tan^{-1}\frac{y}{E}\right). \tag{6.1}$$

This should be compared to our exact result (3.16). Noting that $\lim_{y\to\infty}\alpha^2(iy) = \frac{1}{2}\omega_p^2$, one sees that Δ_M arises from (3.16) if, *ad hoc*, one retains only the last term under the summation, and then replaces the integrand everywhere by its asymptotic form for large y.

In the limit $\omega_p \to \infty$, Δ_M agrees, for all z, with our perfect-conductor result (4.2), which, in this limit, is exact for the ground state. But Δ_M does not contain the shifts Δ^* peculiar to excited states, because for large z it gives the $O(z^{-4})$ Casimir–Polder result for all states. Since the terms dropped and retained in Mavroyannis' approximation all share the same q plane poles, the Δ^* must have been missing from his supposed exact expression as well. As explained in the introduction, this is what one expects in the Lifshitz theory.

Finally, at small distances, Δ_M correctly reproduces the dominant term Δ_{NR} in (4.1), which Mavroyannis was indeed the first to discover. However, (for finite ω_p) there is a discrepancy between Δ_M and the asymptotic form (4.5) of the exact expression, as regards the next-to-leading terms. In Δ_M the next-to-leading term turns out to be of order $\ln z$, while in (4.5) it is of order z^{-1}.

These comparisons taken together suggest that, though (6.1) has many valuable features, it cannot be relied on in detail. More important, in common with the full Lifshitz theory in its present state of development, it cannot deal reliably with excited states.

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