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1977 J. Phys. A: Math. Gen. 10 601

(http://iopscience.iop.org/0305-4470/10/4/022)

J. Phys. A: Math. Gen., Vol. 10, No. 4, 1977. Printed in Great Britain. © 1977

Quantum mechanics of charged particles near a plasma surface

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Received 26 November 1976

Abstract. We consider the interaction between a quantized model of a semi-infinite plasma and a charged non-relativistic particle outside it, allowing fully for relativistic retardation in the electromagnetic field. The choice of gauge, which in the past has occasioned difficulty and imprecision, is elucidated. The Hamiltonian is written down in the strict Coulomb gauge having div $\boldsymbol{A} = 0$ everywhere. It is then transformed canonically to a more popular gauge where div $\boldsymbol{A}$ has a δ-function singularity on the interface, and where the scalar potential is zero in absence of the particle. The effective interaction ('dynamic image potential') is evaluated to second order in $v/\omega_p Z$ but exactly in $\omega_p Z/c$; (v is the particle velocity, Z is distance to interface, ω_p is the plasma frequency). This complements the standard non-relativistic results which hold to all orders in $v/\omega_p Z$ but only in the limit $\omega_p Z/c \to 0$. Contrary to some suggestions, the dominant interaction (when $\omega_p Z/c \gtrsim 1$ and $v/c \ll 1$) is just the image potential $-e^2/4Z$; the leading corrections to this are given.

1. Introduction

The interaction between macroscopic surfaces and systems of charged particles can be considered from at least two distinct though complementary points of view; first, as a problem in condensed-state physics, namely to generalize the elementary image potential by taking account of surface structure and of the excitations of the medium; and second, as in the present paper, as a problem in quantum electrodynamics. The first approach suggests a non-relativistic treatment; by contrast, in the second approach it is more natural to treat at least the electromagnetic field relativistically (Maxwell's equations and Lorentz force rather than just Poisson's equation and the Coulomb force). From the second viewpoint, systems consisting of charged particles are affected by proximity to a medium because they are coupled to the quantized electromagnetic field, whose normal modes in turn are affected by the boundary conditions at the surface. In the simplest case the medium occupies the half-space $z \leq 0$ bounded by the xy plane. In previous papers we have considered such problems for a perfect conductor (Barton 1974, to be referred to as I) and for a simple model of a plasma (Babiker and Barton 1975, to be referred to as II), the latter as a first step to allow for the effects of field penetration into the medium†. In common parlance, we used a quantized

† Experience shows that the safest first approach to this class of problems is the treatment of the simplest explicitly soluble model which incorporates the features of interest; discussions based from the outset on very general formalisms are apt to obscure or even mask a mishandling of the basic physics. Once their assertions can be checked against more transparently obtained results, such formalisms of course come into their own in the treatment of more realistic cases.

hydrodynamic jellium model of a dispersionless plasma, treated in linearized approximation and with infinite-barrier boundary conditions; then the dielectric function is

$$\epsilon(\omega) = 1 - \omega_p^2/\omega^2, \tag{1.1}$$

with ω_p the plasma frequency. (The perfect conductor corresponds to the limit $\omega_p \to \infty$.) In this model all longitudinal modes (those with div $\boldsymbol{E} \neq 0$ inside the medium, all such modes having frequency $\omega = \omega_p$) are totally decoupled from exterior systems, whence we ignore such modes from now on.

In II we managed to deal only with overall-neutral systems (atoms or molecules), for the following reasons connected with the choice of gauge. The plasma and the electromagnetic field in mutual interaction were quantized, in II, via their normal modes, in the special gauge where the scalar potential is zero, so that

$$\begin{aligned} &\boldsymbol{E} = -\dot{\boldsymbol{A}}, \qquad &&\boldsymbol{B} = \operatorname{curl} \boldsymbol{A}; \\ &\operatorname{div} \boldsymbol{A} = 0 \qquad &&\text{for } z \neq 0. \end{aligned} \tag{1.2}$$

This gauge is widely used in surface problems (see for instance Elson and Ritchie 1971, Marvin *et al* 1976). But some modes induce a surface charge density σ and, by Gauss' law, a discontinuity in E_z and A_z at $z = 0$. Therefore div $\boldsymbol{A}$ has a $\delta(z)$-proportional singularity, and since div $\boldsymbol{A}$ is not everywhere zero, this is not the usual Coulomb gauge. On the other hand the standard Hamiltonian method, which tells one how charged particles are coupled to the quantized electromagnetic field, is formulated explicitly in the Coulomb gauge (Schiff 1968, Power 1964, chap. 6). Hence the standard formalism cannot be applied to our problem without further argument. In II we could sidestep the difficulty as regards overall-neutral systems, by appeal to the Power–Zienau transformation to the coupling $-\boldsymbol{E} \cdot \boldsymbol{d}$, with $\boldsymbol{d}$ the electric dipole operator (Power 1964, chap. 8, Power and Zienau 1959, Woolley 1971); but unfortunately this transformation does not, at least in convenient form, apply to charged systems.

The present paper completes the argument of II by extending it to charged particles. In particular, we shall encounter the effects of relativistic retardation and quantum corrections on the so called 'dynamic image potential'; (for a general non-relativistic introduction see Mahan 1973, or Brown and March 1976). The particle charge is denoted by e, the mass by m, the canonical position and momentum coordinates by $\boldsymbol{R}$ and $\boldsymbol{P}$, and the velocity by $\boldsymbol{v} = \dot{\boldsymbol{R}}$. Thus Z is the distance of the particle from the interface. (The units are Gaussian, i.e. $e^2/\hbar c \approx 1/137$ if e is the electronic charge; and we set $\hbar = 1 = c$ except when stressing the presence of $\hbar$ or c.) The particles are treated non-relativistically, but the fields obey Maxwell's equations, so that relativistic retardation is accounted for automatically; it is precisely such retardation which warrants continued interest in the problem, and makes the choice of gauge non-trivial. We shall work formally to second order in m^{-1}. This restricts one to second order in v, i.e. to second order in both the dimensionless parameters v/c and $v/\omega_p Z$. Here it is useful to visualize the hierarchy of distances (in any realistic case): $\hbar/mc \ll v/\omega_p \ll c/\omega_p$; our approximations are valid in the region $Z \gg v/\omega_p$, but without restriction on $\omega_p Z/c$. By contrast, previous non-relativistic calculations of the dynamic image potential take the limit $c \to \infty$ from the outset, and are valid in the region $\hbar/mc \ll Z \ll c/\omega_p$, but without further restrictions on v except $v/c \ll 1$ (i.e. such calculations are then valid mathematically, granted the physical simplifications of the model, whose most important limitation at small distances is its neglect of (spatial) dispersion). Thus, the present calculation and previous ones complement each other in their domains of validity. The non-relativistic approach fully accommodates effects due to the inertia and consequent finite response time of the medium, while the present approach matches these to purely relativistic retardation. In the light of the theory we develop, a unified treatment is certainly possible; but it would be cumbersome, and not transparent enough for a first attempt.

As in II, we confine ourselves to particles which remain outside the medium; our end result is a position- and momentum-dependent effective Hamiltonian which operates on the particle wavefunction (though no longer on the state vector for field and medium). This type of approach to a related problem has been discussed in more detail elsewhere (Barton 1970).

Paper II serves as a more detailed general introduction; we shall draw freely on its notation and results. Section 2 transforms from the gauge defined by (1.2) to the true Coulomb gauge, whose potentials, identified through primes, are determined by

$$\boldsymbol{E} = -\dot{\boldsymbol{A}}' - \operatorname{grad} \phi', \qquad \boldsymbol{B} = \operatorname{curl} \boldsymbol{A}'; \qquad \operatorname{div} \boldsymbol{A}' = 0 \qquad \text{for all } z. \tag{1.3}$$

The scalar potential ϕ' enters as a second-quantized field operator on exactly the same footing as $\boldsymbol{A}'$. In the Coulomb gauge, the correct Hamiltonian H' in presence of the particle can be written down at once. But the couplings which involve ϕ' prove inconvenient in calculation; hence § 3 performs a canonical transformation of H', which eliminates ϕ' in favour of the unretarded ('electrostatic') image potential

$$V_{\text{es}} = -e^2/4Z, \tag{1.4}$$

and which, in all other terms of H', conveniently replaces $\boldsymbol{A}'$ by just the operator $\boldsymbol{A}$ in the more popular original gauge (1.2) already adopted in II. Sections 4.1 and 4.2 calculate the additive corrections to V_{es} to leading (second) order in e and in v; § 4.3 gives the asymptotic form of these corrections in several physically interesting limits; and § 4.4 determines the domain of applicability of our approximations. In particular, it emerges that at low speeds ($v/c \ll 1$) and long range ($\omega_{\text{p}}Z/c \gg 1$) the dominant interaction is V_{es} itself. Section 5 summarizes the results, rewrites them in terms of particle velocities instead of momenta, and compares them to a recent paper by Tomaš and Šunjić (1975), where the contributions from some of the normal modes have been missed, resulting in a wrong suggestion as to the long-range behaviour of the interaction.

2. Normal modes and couplings in the Coulomb gauge

Consider the model plasma and the electromagnetic field in mutual interaction but in absence of any external particle. The Hamiltonian H_0 of this system, and its normal modes using the gauge (1.2), were discussed in II. Introduce a single index λ to specify the modes, i.e. the type of polarization (s-polarized (s), p-polarized (p), or surface-plasmon (sp), longitudinal modes being ignored as explained in § 1); the wavenumber $\boldsymbol{k}$ parallel to the interface; the external wavenumber q normal to the interface; and for partially transmitted s or p waves (with $q > \omega_{\text{p}}$) also the type (1) or (2) of mode. The appropriate combination of sums and integrals over all these labels is denoted by Σ_λ; the mode frequency is ω_λ (for s and p modes, $\omega_\lambda^2 = \omega^2 \equiv (k^2 + q^2)$; for sp modes,

$\omega_\lambda^2=\tilde{\omega}^2\equiv[\frac{1}{2}\omega_p^2+k^2-(\frac{1}{4}\omega_p^4+k^4)^{1/2}])$. Following II, and dropping irrelevant zero-point energies, one has

$$H_0=\sum_\lambda \omega_\lambda a_\lambda^+ a_\lambda, \tag{2.1}$$

$$\boldsymbol{A}(\boldsymbol{r})=\sum_\lambda (a_\lambda \boldsymbol{A}_\lambda(\boldsymbol{r})+a_\lambda^+\boldsymbol{A}_\lambda^*(\boldsymbol{r})). \tag{2.2}$$

The a_λ (a_λ^+) are the usual annihilation (creation) operators, obeying $[a_\lambda, a_{\lambda'}^+]=\delta_{\lambda\lambda'}$, and having the time dependence $\mathrm{e}^{-\mathrm{i}\omega_\lambda t}$ ($\mathrm{e}^{+\mathrm{i}\omega_\lambda t}$) which is not shown explicitly; the $\boldsymbol{A}_\lambda$ are the mode functions given in II for sp modes and for s and p modes having $q>\omega_p$ (partial transmission), by Elson and Ritchie (1971) for $q<\omega_p$ (total reflection), and in I for the perfect-conductor limit $\omega_p\to\infty$. These functions are not displayed in the present paper.

As explained in § 1, in principle we must start by re-expressing the modes in the Coulomb gauge (1.3), where ϕ' obeys Poisson's equation:

$$\nabla^2\phi'=-4\pi\sigma\delta(z)=-\delta(z)(E_z(0+)-E_z(0-))=\delta(z)(\dot{A}_z(0+)-\dot{A}_z(0-)), \tag{2.3}$$

whence the normal-mode functions ϕ_λ' assume the form

$$\phi_\lambda'\sim\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\rho}-k|z|). \tag{2.4}$$

Equation (2.2) is now replaced by

$$\boldsymbol{A}'=\sum(a_\lambda\boldsymbol{A}_\lambda'+a_\lambda^+\boldsymbol{A}_\lambda'^*), \qquad \phi'=\sum(a_\lambda\phi_\lambda'+a_\lambda^+\phi_\lambda'^*); \tag{2.5}$$

the ϕ_λ' are normed so as to obey (2.3) ($\boldsymbol{A}$ being already known at this stage), and $\boldsymbol{A}'$ is determined by

$$\boldsymbol{E}=-\dot{\boldsymbol{A}}=-\dot{\boldsymbol{A}}'-\operatorname{grad}\phi'. \tag{2.6}$$

(Specifically, the surface charge and the functions ϕ_λ' vanish for s modes, and for p-modes of type (2) with $q>\omega_p$.) Note also

$$\dot{\boldsymbol{A}}=-\mathrm{i}\sum\omega_\lambda(a_\lambda\boldsymbol{A}_\lambda-a_\lambda^+\boldsymbol{A}_\lambda^*), \tag{2.7}$$

with similar expressions for any potential in either gauge. In particular, we shall need the time integral of (2.6):

$$\boldsymbol{A}=\boldsymbol{A}'+\mathrm{i}\nabla\sum(a_\lambda\phi_\lambda'-a_\lambda^+\phi_\lambda'^*)/\omega_\lambda. \tag{2.8}$$

When an external particle is present, the total Hamiltonian in Coulomb gauge is

$$H'=H_0+e\phi'(\boldsymbol{R})+(\boldsymbol{P}-e\boldsymbol{A}'(\boldsymbol{R}))^2/2m\equiv H_0+\boldsymbol{P}^2/2m+H_{\mathrm{int}}'. \tag{2.9}$$

From now on, the argument $\boldsymbol{R}$ of the field operators will be suppressed. To see that (2.9) is correct, recall first (Schiff 1968, Power 1964, chap. 6) that in Coulomb gauge the Hamiltonian includes the integral $\frac{1}{2}\int \mathrm{d}^3r\rho(r)\phi'(r)$, where ρ is the sum of the surface charge density $\sigma\delta(z)$ and the charge density $e\delta(\boldsymbol{r}-\boldsymbol{R})$ of the particle; at the same time the right-hand side of (2.3) is augmented by $-4\pi e\delta(\boldsymbol{r}-\boldsymbol{R})$. The integral separates into three terms (all unretarded), as follows: (i) the self-interaction of the particle; this is a constant independent of $\boldsymbol{R}$ and $\boldsymbol{P}$, and for our purposes we can drop it. (ii) Interaction of the medium with itself; this is subsumed into the gauge-invariant Hamiltonian H_0 for medium plus field. (iii) Interaction between particle and medium; this is precisely the term $e\phi'$ in (2.9), written in this asymmetric form purely for convenience, ($\phi'(\boldsymbol{R})$ being the scalar potential at the particle due to the medium: note the absence of any factor $\frac{1}{2}$).

We shall use perturbation theory (to order e^2 and orders $1/m$ and $1/m^2$) to calculate the effective interaction operator between particle and medium; this kind of procedure is discussed in I and II. The coupling $-e\boldsymbol{P}\cdot\boldsymbol{A}'/m$ by itself is easy to handle, since it enters to second order where it is already of order $1/m^2$, so that further corrections of order $1/m$ in the energy denominators can be neglected; in other words these denominators can be approximated by $(-\omega_\lambda)$; (see the comments in § 1 and in § 4.4 about the accuracy). But the coupling $e\phi'$ lacks this simplifying feature; therefore in practice it is incomparably more convenient to proceed via the canonical transformation given in the next section.

3. The canonical transformation

The unwelcome operator ϕ' is eliminated from H' by a suitably chosen canonical transformation U. This idea has been widely used in fixed-source field theory (see for instance Wentzel 1949 or Barton 1963); it has also been applied to the system under discussion, though, as far as the writer knows, only in its non-relativistic version (see for instance Kanazawa 1961, Šunjić *et al* 1972). We chose

$$U=\mathrm{e}^{\mathrm{i}S}, \qquad S=\mathrm{i}e\sum_\lambda (a_\lambda\phi'_\lambda(\boldsymbol{R})-a^+_\lambda\phi'^*_\lambda(\boldsymbol{R}))/\omega_\lambda, \tag{3.1}$$

define

$$\mathrm{e}^{\mathrm{i}S}H'\,\mathrm{e}^{-\mathrm{i}S}\equiv H, \tag{3.2}$$

and exploit the identity, valid for any operator $\mathcal{O}$:

$$\mathrm{e}^{\mathrm{i}S}\mathcal{O}\,\mathrm{e}^{-\mathrm{i}S}=\mathcal{O}+\mathrm{i}[S,\mathcal{O}]+(\mathrm{i}^2/2!)[S,[S,\mathcal{O}]]+\ldots. \tag{3.3}$$

The commutation rules lead straightforwardly to the following results:

$$\mathrm{e}^{\mathrm{i}S}(H_0+e\phi')\,\mathrm{e}^{-\mathrm{i}S}=H_0-e^2\sum_\lambda|\phi'_\lambda|^2/\omega_\lambda=H_0+V_{\mathrm{es}}, \tag{3.4}$$

where the last step, with V_{es} defined by (1.4), follows by direct evaluation once the ϕ'_λ are determined as explained in § 2. One can anticipate this result by observing: (i) that for a strictly immobile external charge, i.e. in the limit $m\to\infty$, the sum in (3.4) is the only interaction which survives, and that it itself is unaffected by taking this limit; and (ii) that in this limit the model displays perfect screening, as discussed further near the end of this section. Next,

$$\begin{aligned}\mathrm{e}^{\mathrm{i}S}\boldsymbol{P}\,\mathrm{e}^{-\mathrm{i}S}&=\boldsymbol{P}-\mathrm{i}e\nabla\sum(a_\lambda\phi'_\lambda-a^+_\lambda\phi'^*_\lambda)/\omega_\lambda+\tfrac{1}{2}\mathrm{i}e^2\sum(\phi'^*_\lambda\nabla\phi'_\lambda-\phi'_\lambda\nabla\phi'^*_\lambda)/\omega^2_\lambda\\&=\boldsymbol{P}-\mathrm{i}e\nabla\sum(a_\lambda\phi'_\lambda-a^+_\lambda\phi'^*_\lambda)/\omega_\lambda.\end{aligned} \tag{3.5}$$

The last sum in the second expression vanishes; this can be seen either by explicit evaluation (by azimuthal symmetry under the integration $\int \mathrm{d}^2k$ included in Σ_λ, and in view of the form (2.4) of the ϕ'_λ); or more generally by invariance under time reversal T, since this term is an addend to $\boldsymbol{P}$ but nevertheless even under T. Finally,

$$\mathrm{e}^{\mathrm{i}S}\boldsymbol{A}'\,\mathrm{e}^{-\mathrm{i}S}=\boldsymbol{A}'-e\sum(\phi'_\lambda\boldsymbol{A}'^*_\lambda+\phi'^*_\lambda\boldsymbol{A}'_\lambda)/\omega_\lambda=\boldsymbol{A}', \tag{3.6}$$

where the sum vanishes for reasons similar to those just discussed. Now (3.5) and (3.6) entail

$$\mathrm{e}^{\mathrm{i}S}(\boldsymbol{P}-e\boldsymbol{A}')\,\mathrm{e}^{-\mathrm{i}S}=\boldsymbol{P}-e(\boldsymbol{A}'+\mathrm{i}\nabla\sum(a_\lambda\phi'_\lambda-a^+_\lambda\phi'^*_\lambda)/\omega_\lambda);$$

but (2.8) identifies the right-hand side as just $(\boldsymbol{P}-e\boldsymbol{A})$, whence our end result is

$$H=H_0+V_{es}+(\boldsymbol{P}-e\boldsymbol{A})^2/2m\equiv H_0+\boldsymbol{P}^2/2m+V_{es}+H_{int}, \tag{3.7}$$

as promised in § 1. No approximations have been made so far.

The Hamiltonian H is our starting point for calculations. V_{es} acts only on the particle wavefunction but not on the normal modes; the latter can be excited only through the interaction $H_{int}=-e\boldsymbol{P}\cdot\boldsymbol{A}/m+e^2\boldsymbol{A}^2/2m$. For instance, if one aims to calculate the overall emission of photons and surface plasmons induced by charged particles, and if the effect of V_{es} on the particle motion is negligible, then one can safely start from (3.7) but with V_{es} omitted. Just this has been done recently by Marvin *et al* (1976). However, to describe the time evolution of the fields in such a process, correctly and without violating causality, the full Hamiltonian would be needed.

The unretarded polarization of the medium is allowed for automatically by the transformation U; for instance, the 'no-excitation' eigenstate $|0\rangle$ of $(H-H_{int})=(H_0+V_{es})$ is given in terms of the 'no-excitation' eigenstate $|0'\rangle$ of $(H'-H'_{int})=H_0$, and of the other eigenstates of H_0, by $|0\rangle=\exp(-\mathrm{i}S)|0'\rangle$.

That V_{es} happens to be the image potential for a perfect conductor merely reflects a peculiarity of our model plasma, namely that for a truly stationary charge it gives perfect screening. This in turn follows from the neglect of hydrodynamic pressure; it is implicit in the absence of any wavenumber dependence of the dielectric function (1.1), and in its pole at zero frequency. These features are not essential to the argument so far, and were adopted purely to simplify the calculations which follow.

4. Perturbation calculation

The effects of H_{int} in (3.7) are evaluated by perturbation theory; to order e^2 they simply add to V_{es}, the unperturbed states being the eigenstates of $H_0+\boldsymbol{P}^2/2m$. The calculation proceeds along almost the same lines as (for neutral atoms) in II; we indicate only the outlines, and points where the technicalities differ appreciably. (We have checked by explicit calculation that for neutral atoms the present method reproduces the results of II.) As in I and II, we reject systematically all (including divergent) terms independent of Z, and all contact terms proportional to $\delta(Z)$ or its derivatives. Recall from II the notations $\omega^2\equiv k^2+q^2$;

$$Q(q)\equiv(q^2-\omega_p^2)^{1/2}, \tag{4.1}$$

defined with a branch cut along the real axis between $\pm\omega_p$, and with $\operatorname{Im} Q>0$ when $\operatorname{Im} q>0$; also

$$\alpha^2(q)\equiv q(q-Q), \qquad \alpha^2(\mathrm{i}y)=y[(y^2+\omega_p^2)^{1/2}-y]; \tag{4.2}$$

and write $\boldsymbol{P}_\parallel^2\equiv P_x^2+P_y^2$, $P_3^2\equiv P_z^2$.

4.1. *Second-order perturbation* $\Delta^{(2)}$

The second-order shift due to $-e\boldsymbol{P}\cdot\boldsymbol{A}/m$ is approximated by taking the energy denominators as $-\omega_\lambda$, i.e. by neglecting recoil corrections. The accuracy of this step is discussed in § 4.4. One finds,

$$\Delta^{(2)}=-(e^2/m^2)\sum_\lambda|\boldsymbol{A}_\lambda\cdot\boldsymbol{P}|^2/\omega_\lambda\equiv\Delta_s^{(2)}+\Delta_p^{(2)}+\Delta_{sp}^{(2)}, \tag{4.3}$$

distinguishing the contributions from the three different kinds of normal modes. For $\Delta_s^{(2)}$ one obtains straightforwardly

$$\Delta_s^{(2)} = -\frac{e^2}{2\pi\omega_p^2 m^2}\int_0^\infty dk\, k\int_{-\infty}^\infty dq\; e^{2iqZ}\frac{(q-Q)^2}{\omega^2}\left(\frac{1}{2}\boldsymbol{P}_\parallel^2\right), \tag{4.4}$$

where the q-contour runs just above the real axis, i.e. just above the cut due to Q. The contour can be closed along the upper semicircle at infinity, and the q-integral is determined by the residue of the pole at $\omega^2 = 0$, i.e. at $q = ik$:

$$\Delta_s^{(2)} = \frac{e^2}{2\omega_p^2 m^2}\int_0^\infty dk\; e^{-2kZ}[(k^2+\omega_p^2)^{1/2}-k]^2\left(\frac{1}{2}\boldsymbol{P}_\parallel^2\right). \tag{4.5}$$

The analogue of (4.4) for $\Delta_p^{(2)}$ is

$$\Delta_p^{(2)} = -\frac{e^2}{2\pi\omega_p^2 m^2}\int_0^\infty dk\, k\int_{-\infty}^\infty dq\; e^{2iqZ}\frac{(q-Q)^2}{\omega^4}\left(1-\frac{2qQ}{\omega^2-\alpha^2}\right)(k^2P_3^2-q^2\tfrac{1}{2}\boldsymbol{P}_\parallel^2). \tag{4.6}$$

Actually one operator P_3 should be written on the left and the other on the right of the P_3^2-proportional term, but for brevity we shall not always observe this. The q-integrand in (4.6) has a double pole at $q = ik$; it also has a pole at $\omega^2 = \alpha^2$, whose contribution turns out precisely to cancel $\Delta_{sp}^{(2)}$, in the manner familiar from II. One finds eventually

$$\Delta_p^{(2)} + \Delta_{sp}^{(2)} = -\frac{e^2}{2\omega_p^2 m^2}\int_0^\infty dk\; e^{-2kZ}\{[\omega_p^2 + 2k(k^2+\omega_p^2)^{1/2}]P_3^2 + [2k(k^2+\omega_p^2)^{1/2}]\tfrac{1}{2}\boldsymbol{P}_\parallel^2\}. \tag{4.7}$$

Combining (4.6) and (4.7), changing to a dimensionless integration variable, and reverting to conventional units, one obtains finally

$$\begin{aligned}\Delta^{(2)} &= \frac{e^2\omega_p}{2m^2c^3}\int_0^\infty dx\; e^{-(2\omega_p Z/c)x}\{-[1+2x(x^2+1)^{1/2}]P_3^2 + [2x^2+1-4x(x^2+1)^{1/2}]\tfrac{1}{2}\boldsymbol{P}_\parallel^2\}\\ &\equiv \frac{1}{2m}\left(P_3F_3\left(\frac{2\omega_p Z}{c}\right)P_3 + F_\parallel\left(\frac{2\omega_p Z}{c}\right)\frac{1}{2}\boldsymbol{P}_\parallel^2\right).\end{aligned} \tag{4.8}$$

4.2. *First-order perturbation* $\Delta^{(1)}$

The first-order shift, i.e. the vacuum expectation value of $e^2\boldsymbol{A}^2/2m$, is

$$\Delta^{(1)} = (e^2/2m)\sum_\lambda |\boldsymbol{A}_\lambda|^2 \equiv \Delta_s^{(1)} + \Delta_p^{(1)} + \Delta_{sp}^{(1)}. \tag{4.9}$$

One finds

$$\Delta_s^{(1)} = \frac{e^2}{4\pi\omega_p^2 m}\int_0^\infty dk\, k\int_{-\infty}^\infty dq\; e^{2iqZ}\frac{(q-Q)^2}{\omega}. \tag{4.10}$$

This q-integrand has a cut, due to ω^{-1}, from $q=\mathrm{i}k$ to $q=+\mathrm{i}\infty$, and deformation of the contour yields

$$\Delta_{\mathrm{s}}^{(1)}=-\frac{e^2}{2\pi\omega_{\mathrm{p}}^2 m}\int_0^\infty \mathrm{d}k\, k\int_k^\infty \mathrm{d}y\, \mathrm{e}^{-2yZ}\frac{[(y^2+\omega_{\mathrm{p}}^2)^{1/2}-y]^2}{(y^2-k^2)^{1/2}}.$$

By using $\int_0^\infty \mathrm{d}k \int_k^\infty \mathrm{d}y\ldots=\int_0^\infty \mathrm{d}y\int_0^y \mathrm{d}k\ldots$, the k-integration is performed first, and yields

$$\Delta_{\mathrm{s}}^{(1)}=-\frac{e^2}{2\pi\omega_{\mathrm{p}}^2 m}\int_0^\infty \mathrm{d}y\, \mathrm{e}^{-2yZ}y[(y^2+\omega_{\mathrm{p}}^2)^{1/2}-y]^2. \tag{4.11}$$

The p-contribution analogous to (4.10) is

$$\Delta_{\mathrm{p}}^{(1)}=\frac{e^2}{4\pi\omega_{\mathrm{p}}^2 m}\int_0^\infty \mathrm{d}k\, k\int_{-\infty}^\infty \mathrm{d}q\, \mathrm{e}^{2\mathrm{i}qZ}(q-Q)^2\left(1-\frac{2qQ}{\omega^2-\alpha^2}\right)\left(\frac{\omega^2-2q^2}{\omega^3}\right). \tag{4.12}$$

This q-contour cannot be deformed as for $\Delta_{\mathrm{s}}^{(1)}$, because the singularity due to ω^{-3} would lead to a y-integral diverging at its lower limit. The difficulty is circumvented as follows. Invert the order of integration, write $\int_0^\infty \mathrm{d}k\, k\ldots=\int_{|q|}^\infty \mathrm{d}\omega\, \omega\ldots$, and try to perform the ω-integration. Taking partial fractions one faces

$$\int_{|q|}^\infty \mathrm{d}\omega\left[1-\frac{2q^2}{\omega^2}\left(1+\frac{2qQ}{\alpha^2}\right)+\frac{2qQ}{\omega^2-\alpha^2}\left(-1+\frac{2q^2}{\alpha^2}\right)\right]. \tag{4.13}$$

The crucial observation is that any entire function of q and in particular any constant emerging from this integration fails to contribute, since it gives a q-integrand wholly free of singularities in the upper-half q-plane. Thus, anticipating the q-integration, we have the equivalence (dropping a constant, albeit infinite):

$$\int_{|q|}^\infty \mathrm{d}\omega=(\infty-|q|)\Rightarrow -|q|;$$

comparing this to

$$\int_{|q|}^\infty \mathrm{d}\omega\, q^2/\omega^2=|q|$$

we see that in (4.13) we may make the replacement

$$q^2/\omega^2\Rightarrow -1.$$

After this replacement the original order of the integrations is restored, and instead of (4.12) one obtains

$$\Delta_{\mathrm{p}}^{(1)}=\frac{e^2}{4\pi\omega_{\mathrm{p}}^2 m}\int_0^\infty \mathrm{d}k\, k\int_{-\infty}^\infty \mathrm{d}q\, \mathrm{e}^{2\mathrm{i}qZ}\frac{(q-Q)^2}{\omega}\left[1+2\left(1+\frac{2qQ}{\alpha^2}\right)+\frac{2qQ}{\omega^2-\alpha^2}\left(-1+\frac{2q^2}{\alpha^2}\right)\right]. \tag{4.14}$$

The q-contour can now be deformed as was done for $\Delta_{\mathrm{s}}^{(1)}$. The contribution from the pole at $\omega^2=\alpha^2$ cancels $\Delta_{\mathrm{sp}}^{(1)}$ as expected. The contribution from the branch cut due to

ω^{-1} is dealt with as before. Combining $(\Delta_p^{(1)}+\Delta_{sp}^{(1)})$ with $\Delta_s^{(1)}$, and reverting to conventional units, one obtains the end result

$$\Delta^{(1)}=\frac{e^2\hbar\omega_p^2}{\pi mc^3}\int_0^\infty dx\, e^{-(2\omega_p Z/c)x}\{2x^2[(x^2+1)^{1/2}-x] + (x^2+1)^{1/2}[x(x^2+1)^{1/2}+x^2]^{1/2}\tan^{-1}[x(x^2+1)^{1/2}+x^2]^{1/2}\}. \tag{4.15}$$

4.3. *Asymptotics*

$\Delta^{(2)}$ and $\Delta^{(1)}$ are given above as Laplace transforms with respect to the dimensionless variable $(2\omega_p Z/c)$. Hence the non-relativistic limit $c\to\infty$ automatically coincides with the short-distance limit, and the perfect-conductor limit $\omega_p\to\infty$ coincides with the long-distance limit; but neither limit in one of these pairings is compatible with either limit in the other pairing.

For small values of $2\omega_p Z/c$, the integrands in (4.8) and (4.15) are approximated asymptotically by expanding them, apart from the exponential, in descending powers of x. This yields

$$\Delta^{(2)}=-\frac{e^2}{4m^2\omega_p^2 Z^3}\left\{P_3\left[1+2\left(\frac{\omega_p Z}{c}\right)^2\right]P_3 + \left[1+\left(\frac{\omega_p Z}{c}\right)^2\right]\frac{1}{2}\boldsymbol{P}_\parallel^2\right\}+(\text{terms remaining finite as } Z\to 0), \tag{4.16}$$

$$\Delta^{(1)}=\frac{e^2\hbar}{2^{1/2}4m\omega_p^2 Z^3}\left[1+\frac{5}{4}\left(\frac{\omega_p Z}{c}\right)^2\right] + \frac{e^2\hbar\omega_p}{mc^3}\times(\text{terms of O(1) or O}(\ln \omega_p Z/c)\text{ as } Z\to 0). \tag{4.17}$$

For large values of $2\omega_p Z/c$, the asymptotic expansions are in ascending powers of x, and yield

$$\Delta^{(2)}=-\frac{e^2}{4m^2c^2Z}\left\{P_3\left[1+\frac{c}{\omega_p Z}+O\left(\frac{c}{\omega_p Z}\right)^2\right]P_3-\left[1-2\frac{c}{\omega_p Z}+O\left(\frac{c}{\omega_p Z}\right)^2\right]\frac{1}{2}\boldsymbol{P}_\parallel^2\right\}, \tag{4.18}$$

$$\Delta^{(1)}=\frac{e^2\hbar}{4\pi mcZ^2}\left[1+\frac{8}{3}\frac{c}{\omega_p Z}+O\left(\frac{c}{\omega_p Z}\right)^2\right]. \tag{4.19}$$

4.4. *Accuracy of the no-recoil approximation to* $\Delta^{(2)}$

In the energy denominators entering $\Delta^{(2)}$ we have ignored recoil energies of the type $-[(\boldsymbol{P}-\boldsymbol{k})^2-\boldsymbol{P}^2]/2m$ and similar q-dependent terms, and must now check under what conditions these are negligible compared to $-\omega_\lambda$. The crucial observation is that in the regions dominating Laplace integrals like (4.5) and (4.7), k is effectively of order of magnitude $1/Z$; similarly in the preceding q-integrals, q is of order $1/Z$. (For instance, factors of k or q under the integrals can be replaced by $\partial/\partial Z$ acting on the end result.) For simplicity we present the argument in terms of k alone, and correspondingly ignore any q-dependence of ω_λ. The short- and long-range regimes must be considered separately, and we need the normal-mode frequencies quoted just above equation (2.1).

For small Z, i.e. large $k \sim 1/Z$, the s and p modes have $\omega_\lambda = \omega \sim k$. Then $Pk/m \ll \omega_\lambda$ implies only $v/c \ll 1$ which is assumed anyway; and $k^2/m \ll \omega_\lambda$ implies $\hbar/mcZ \ll 1$, which is a trivial condition in practice since it demands only that $Z \gg$(Compton wavelength). But for surface plasmon modes, $\omega_\lambda = \tilde{\omega} \sim \sqrt{\frac{1}{2}}\omega_p$. Then $k^2/m \ll \omega_\lambda$ implies $Z^2 \gg \hbar/m\omega_p$; since $\hbar\omega_p$ is roughly comparable to typical atomic energies e^2/a_B ($a_B = \hbar^2/m_e e^2$ is the Bohr radius; m_e is the electron mass), this demands only $Z \gg (m_e/m)^{1/2} a_B$. Finally, $Pk/m \ll \omega_\lambda$ now implies

$$Z \gg v/\omega_p. \tag{4.20}$$

In cases of practical interest, (4.20) is the operative condition.

For large Z, i.e. small $k \sim 1/Z$, all modes have frequencies $\omega_\lambda \sim k \sim 1/Z$, and a repetition of the above argument demands only $v/c \ll 1$ and $\hbar/mcZ \ll 1$, which for large Z impose no new conditions. Thus we have substantiated the remarks about accuracy in § 1: our results are valid to second order in $v/\omega_p Z$ but are exact in $\omega_p Z/c$.

5. Summary and discussion

5.1. Summary

We have found that to the accuracy stated at the end of § 4.4 the behaviour of charged particles outside the medium is governed by the effective Hamiltonian

$$H_{\text{eff}} = \frac{1}{2m}\boldsymbol{P}^2 - \frac{e^2}{4Z} + \Delta^{(1)}(Z) + \frac{1}{2m}P_3 F_3(Z) P_3 + \frac{1}{2m}F_\parallel(Z)\tfrac{1}{2}\boldsymbol{P}_\parallel^2. \tag{5.1}$$

$\Delta^{(1)}$ is given by (4.15), and its asymptotics by (4.17) and (4.19); the momentum-dependent terms (which constitute $\Delta^{(2)}$) by (4.8), and their asymptotics by (4.16) and (4.18). Thus for short distances

$$H_{\text{eff}} \approx \frac{1}{2m}\boldsymbol{P}^2 - \frac{e^2}{4Z} + \frac{e^2\hbar}{2^{1/2}4m\omega_p Z^3} - \frac{e^2}{4m^2\omega_p^2 Z^3}\left(P_3^2 + \frac{1}{2}\boldsymbol{P}_\parallel^2\right), \tag{5.2}$$

and for large distances

$$H_{\text{eff}} \approx \frac{1}{2m}\boldsymbol{P}^2 - \frac{e^2}{4Z} + \frac{e^2\hbar}{4\pi mcZ^2} - \frac{e^2}{4m^2c^2Z}\left(P_3^2 - \frac{1}{2}\boldsymbol{P}_\parallel^2\right). \tag{5.3}$$

Note that the $\boldsymbol{P}_\parallel^2$-proportional energy changes sign with increasing Z. (This term in (5.3) checks with the perfect-conductor result obtainable as a limiting case from Barton (1970, equations (2.30)–(2.32)); in (5.2) it checks with calculations setting $c \to \infty$ *ab initio* (Šunjić *et al* 1972, Ray and Mahan 1972), bearing in mind the question of sign discussed in § 5.3 below. Similar checks are verified by the leading terms of $\Delta^{(1)}$ in equation (4.19) (see I) and equation (4.17).)

Inspection for factors of $\hbar$, c, and ω_p shows that $\Delta^{(1)}$ is a purely quantum correction vanishing as $\hbar \to 0$; and that the momentum-dependent terms $\Delta^{(2)}$ are classical retardation corrections, due at small distances to the finite response speed of the medium, and at large distances to the finite value of c.

5.2. *Orders of magnitude*

Denote the order of magnitude of P/m by v. At short distances, $|\Delta^{(1)}/\Delta^{(2)}|$ is of order $\hbar\omega_p/mv^2$, which in principle can be large or small, but most often will be small. Moreover $|\Delta^{(2)}/V_{es}|$ is of order $(v/\omega_p Z)^2$, necessarily small in the domain (4.20), where V_{es} is consequently dominant.

At long distances, $|\Delta^{(1)}/\Delta^{(2)}|$ is of order $\hbar c/mv^2 Z=(c/\omega_p Z)(\hbar\omega_p/mv^2)$; the first factor is small, and the second generally also small. But $|\Delta^{(2)}/V_{es}|$ is of order v^2/c^2, i.e. small for all non-relativistically moving particles.

Consequently, throughout the region $Z \gg v/\omega_p$, the dominant term is V_{es}; and apart from very exceptional cases, the next most important energy is $\Delta^{(2)}$, rather than the quantum correction $\Delta^{(1)}$. Hence it is worth considering a limit in which $\Delta^{(1)}$ is dropped, and the remainder of H_{eff} is regarded as a classical Hamiltonian with commuting canonical variables $\boldsymbol{R}$ and $\boldsymbol{P}$. In some cases it may be possible to simplify still further by treating the particle as if it was moving along a prescribed trajectory; then H_{eff} yields information about the overall energy transfer to field and medium, while for a detailed account of the polarization one would have to revert to equation (3.7), as the first step of a Born–Oppenheimer treatment.

5.3. *Velocity dependence*

For the classical limit just envisaged it is instructive to express H_{eff} in terms of velocities rather than momenta. Because the interaction $\Delta^{(2)}$ is momentum dependent, it enters into the relation $\dot{\boldsymbol{R}}=\partial H/\partial \boldsymbol{P}$; from (5.1) one finds, to order e^2,

$$\dot{\boldsymbol{R}}_\parallel \equiv \boldsymbol{v}_\parallel = \frac{1}{m}\boldsymbol{P}_\parallel(1+\tfrac{1}{2}F_\parallel(Z)), \qquad \dot{Z}\equiv v_3=\frac{1}{m}P_3(1+F_3(Z)),$$
$$\boldsymbol{P}_\parallel = m\boldsymbol{v}_\parallel(1-\tfrac{1}{2}F_\parallel(Z)), \qquad P_3=mv_3(1-F_3(Z)), \tag{5.4}$$

$$\mathrm{H}_{eff}=\tfrac{1}{2}m\boldsymbol{v}^2-\frac{e^2}{4Z}+\Delta^{(1)}(Z)-\tfrac{1}{2}mF_3(Z)v_3^2-\tfrac{1}{2}mF_\parallel(Z)\tfrac{1}{2}\boldsymbol{v}_\parallel^2. \tag{5.5}$$

Note the opposite signs of the velocity-dependent interactions in (5.5) and the corresponding momentum-dependent interactions in (5.1). The same transformation gives the velocity-dependent counterparts of (5.2) and (5.3).

5.4. *Comparison with other work*

The standard non-relativistic ($c\to\infty$) and adiabatic (Born–Oppenheimer) expression for the total interaction of particles moving perpendicularly to the interface is (Šunjić *et al* 1972, Ray and Mahan 1972)

$$-\frac{1}{2}e^2\int_0^\infty \mathrm{d}k\,\frac{\mathrm{e}^{-2kZ}}{1+2(kv_3/\omega_p)^2}, \tag{5.6}$$

with possibly an upper cut-off irrelevant in this context. The integral in (5.6) embraces V_{es} and $\Delta^{(2)}$, and for a dispersionless plasma derives wholly from surface plasmons. When expanded in powers of v_3, the first two terms agree with (5.2), bearing in mind the apparent sign change explained in the preceding subsection. Of course (5.6) continues to apply for $Z \lesssim v/\omega_p$, where our own no-recoil approximation breaks down.

Tomaš and Šunjić (1975) have tried to generalize (5.6) to the relativistically-retarded domain $Z \gtrsim c/\omega_p$. They start correctly, and remain, in the Coulomb gauge, and drop $\Delta^{(1)}$ as is appropriate in a classical approximation; but even in the relativistic calculation they follow Ritchie (1972) in retaining only the contribution from surface plasmons. To order v^2, and for $Z\omega_p/c \gg 1$, their equation (48) implies the effective interaction

$$-\frac{e^2 c}{8\omega_p Z^2}+\frac{e^2}{Z}\frac{v^2}{c^2}\left(\frac{3}{2}-9\frac{c}{\omega_p Z}+\ldots\right).$$

But for large Z, the contribution from surface plasmons no longer dominates the contribution from s and p modes, so that this expression is unwarranted. Indeed comparison with (5.3) shows it to be wrong; the true dominant term is the elementary image potential $-e^2/4Z$.

Acknowledgments

The writer welcomes this opportunity to acknowledge useful discussions with Dr M Babiker and Professor H Grotch.

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