

Dipoles induced by physical adsorption*

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Expressions are derived for the induced dipole of a spherical atom physically adsorbed on a solid, by the use of perturbation theory. The theory applies to conducting as well as nonconducting solids. It is found that, in all cases, the induced dipole points away from the solid. Various approximations are given and the results are compared with those treated by the image method.

I. INTRODUCTION

Last year two papers appeared on dispersion-induced dipoles. One of these, by Antoniewicz,¹ treated an atom interacting with its electrostatic image field in a classical metal. The other, by Crowell,² considered the moment induced in an atom by the dispersion (van der Waals) interaction with another atom. Both authors used a simple variational procedure. Antoniewicz found that the induced dipole points away from the surface; Crowell's result predicted that the induced dipoles of the two atoms point towards each other. The work function of a metal appears to be correlated with the direction of the dipole moment induced in the adsorbed atom.¹

In this paper we present a unified treatment of the dipole induced in physical adsorption, applicable both to conducting and dielectric solids. The method is based on perturbation theory in which both the atom and the solid are treated quantum mechanically, although a classical analogy is used to interpret the results.

II. DEVELOPMENT

A. Perturbation

Starting with the Raleigh-Schrödinger time-independent perturbation theory, we evaluate the dipole moment of the adsorbed atom using wave functions correct to second order. The first-order term drops out because of electrical neutrality of the unperturbed states of the atom and the solid. The interaction is taken to be

$$\hat{V}(Z_0) = \int d\vec{r} \int d\vec{R} \frac{\hat{\rho}(\vec{r})\hat{\rho}(\vec{R})}{|\vec{r} - \vec{R} - \vec{Z}_0|}, \quad (1)$$

where $\rho(\vec{r})$ and $\rho(\vec{R})$ are, respectively, the charge densities in the atom and in the solid. The center of the atomic coordinate \vec{r} is the center of the atom. \vec{Z}_0 is the vector from the center of the atom to the nearest point on the surface; the latter point is the origin of solid coordinate \vec{R} . The common Z axis points from the atom towards the solid along the perpendicular. The induced dipole has only a Z component by symmetry. It has the form

$$\mu = \int d\vec{r}'' \int d\vec{r}' \int d\vec{r} \int d\vec{R}' \int d\vec{R} \sum_i' \sum_k' \sum_K' [\hat{\rho}(\vec{r}'')\hat{Z}''']_{0i} \rho_{ik}(\vec{r}) \rho_{k0}(\vec{r}') \rho_{0K}(\vec{R}) \rho_{K0}(\vec{R}') \times [|\vec{r} - \vec{Z}_0 - \vec{R}| |\vec{r}' - \vec{Z}_0 - \vec{R}'| \epsilon_i(\epsilon_k + E_k)]^{-1} + c. c., \quad (2)$$

where the i, k refer to the states of the atom; the K refer the states of the solid; the ϵ and E are, respectively, excitation energies of atom and solid. The prime on each \sum denotes that the corresponding ground state is excluded from the summation.

In order to interpret the matrix elements for the solid in this expression we consider first the response of the solid to a classical oscillating charge.

B. Response to classical oscillating charge

The potential due to an oscillating unit charge at the point \vec{r}' oscillating with a frequency ω is

$$X(\vec{r}; \vec{r}', \omega) = \frac{1}{\hbar} \int d\vec{R}' \int d\vec{R} \frac{1}{|\vec{r} - \vec{Z}_0 - \vec{R}| |\vec{r}' - \vec{R}' - \vec{Z}_0|} \sum_N' \left(\frac{\rho_{0N}(\vec{R})\rho_{N0}(\vec{R}')}{\omega - \omega_N - i\xi} - \frac{\rho_{N0}(\vec{R})\rho_{0N}(\vec{R}')}{\omega + \omega_N - i\xi} \right), \quad (3)$$

where $\omega_N = E_N/\hbar$. This expression can be obtained using first-order time-dependent perturbation theory.

If we treat the solid as a macroscopic continuum, then classical electromagnetic theory tells us that this result must be due to an image charge at $2\vec{Z}_0 + \vec{r}'$,

where $\vec{r}' = X'\vec{i} + Y'\vec{j} - Z'\vec{k}$.
From this we obtain

$$-\frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 1} \frac{1}{|\vec{r} - 2\vec{Z}_0 - \vec{r}'|} = X(\vec{r}; \vec{r}'; \omega). \quad (4)$$

The quantity $X(\vec{r}; \vec{r}'; \omega)$, which one might call the potential susceptibility, resembles closely the charge-density susceptibility as defined by Linder and Rabenold.³ Our goal is to express μ in terms of X and thereby in terms of ϵ , the dielectric constant of the solid.

C. μ in terms of ϵ

We define a transition charge-density susceptibility $\chi_{i0}(\vec{r}; \vec{r}'; \omega)$ by the relation

$$\chi_{i0}(\vec{r}; \vec{r}'; \omega) = \lim_{\xi \rightarrow 0} \frac{1}{\hbar} \sum_k' \left(-\frac{\rho_{ik}(\vec{r})\rho_{k0}(\vec{r}')}{\omega + \omega_k - i\xi} + \frac{\rho_{0k}(\vec{r}')\rho_{ki}(\vec{r})}{\omega - \omega_k - i\xi} \right). \quad (5)$$

This is a generalization of the ordinary charge-density susceptibility $\chi(\vec{r}; \vec{r}'; \omega)$ as defined by Eq. (11) of Ref. 3. We now write Eq. (2) in the form

$$\mu = -\frac{\hbar}{2\pi} \int d\vec{r}'' \int d\vec{r}' \int d\vec{r} \frac{1}{|\vec{r} - 2\vec{Z}_0 - \vec{r}'|} \int_0^\infty d\xi \frac{\epsilon(-i\xi) - 1}{\epsilon(-i\xi) + 1} \sum_i' [\hat{\rho}(\vec{r}'')\hat{Z}'']_{0i} \chi_{i0}(\vec{r}; \vec{r}'; -i\xi). \quad (8)$$

This expression is generally valid for an arbitrary molecule and arbitrary solid within the macroscopic continuum approximation. Deviations can be expected for small Z_0 values owing to the structure of the surface.

To proceed, we expand the Coulomb potential $|\vec{r} - 2\vec{Z}_0 - \vec{r}'|^{-1}$ in a Taylor series in \vec{r} and \vec{r}' . For an atom the first surviving term is

$$\mu = -\frac{3\hbar}{16\pi Z_0^4} \int_0^\infty d\xi \frac{\epsilon(-i\xi) - 1}{\epsilon(-i\xi) + 1} \int d\vec{r}'' \int d\vec{r}' \int d\vec{r} \sum_i' \frac{[\hat{\rho}(\vec{r}'')\hat{Z}'']_{0i}}{\epsilon_i} \chi_{i0}(\vec{r}; \vec{r}'; -i\xi) \times (z^2 z' + 2zx'x' + 2xz'x' - x^2 z' + z z'^2 - z x'^2). \quad (9)$$

At this point we will use the independent-particle approximation for the electrons in the atom. Then, in closure,

$$\mu = -\frac{3e^3}{4\pi Z_0^4 \hbar} \sum_n (z^4 + z^2 x'^2)_n \int_0^\infty d\xi \frac{\epsilon(-i\xi) - 1}{(\omega_a^2 + \xi^2)[\epsilon(-i\xi) - 1]}, \quad (10)$$

where e is the magnitude of the electronic charge, n designates an expectation value over the n th ground-state orbital, and ω_a is the effective excitation frequency of the atom. It is apparent that the sign of μ will depend only on the sign of the dielectric function.

III. SEMIEMPIRICAL RESULTS

The dielectric function can be roughly approximated by the expression

$$\frac{\epsilon(-i\xi) - 1}{\epsilon(-i\xi) + 1} = \frac{a}{b^2 + \xi^2}, \quad (11)$$

$$\mu = \frac{\hbar}{2\pi} \int d\vec{r}'' \int d\vec{r}' \int d\vec{r} \sum_i' \frac{[\hat{\rho}(\vec{r}'')\hat{Z}'']_{0i}}{\epsilon_i} \times \int d\xi \chi_{i0}(\vec{r}; \vec{r}'; -i\xi) X(\vec{r}; \vec{r}'; -i\xi), \quad (6)$$

which may be verified using the relation

$$\chi(\vec{r}; \vec{r}'; -i\xi) = \frac{2}{\pi} \int_0^\infty \frac{\omega \chi''(\vec{r}; \vec{r}'; \omega)}{\omega^2 + \xi^2} d\omega,$$

which relates the susceptibility $\chi(-i\xi)$ along the imaginary axis to the imaginary part of the susceptibility, $\chi''(\omega)$, along the real axis. The latter is defined as

$$\chi''_{i0}(\vec{r}; \vec{r}'; \omega) = \frac{\pi}{\hbar} \sum_k [-\rho_{0k}(\vec{r}')\rho_{ki}(\vec{r})\delta(\omega - \omega_k) + \rho_{ik}(\vec{r})\rho_{k0}(\vec{r}')\delta(\omega + \omega_k)]. \quad (7)$$

Similar considerations hold for X . In this development we take the wave functions to be real. Accordingly χ and X are both real along the imaginary frequency axis. Combining (6) and (4) yields

where a and b are constants. For a crystalline solid made up of harmonic oscillators $a = 2\pi N_0 \times \alpha_0(0)\omega_0^2$ and $b^2 = \omega_0^2 + \frac{1}{3}a$, where N_0 is the number of oscillators per unit volume, $\alpha_0(0)$ is the polarizability at zero frequency, and ω_0 the natural frequency of an isolated oscillator. For a metal, within random-phase approximation, $a = b^2 = \frac{1}{2}\omega_p^2$, where ω_p is the plasma frequency.⁴ The form of Eq. (11) permits ready integration of Eq. (10), and yields

$$\mu = -\frac{3}{8} \frac{e^3}{Z_0^4 \hbar} \sum_n (z^4 + z^2 x'^2)_n \frac{a}{b\omega_a(\omega_a + b)}. \quad (12)$$

The sign here indicates that the dipole points away from the surface. Even if a more realistic model were used for the dielectric solid the sign would be the same, as will be seen in Sec. IV.

For atoms

$$\sum_n (z^4 + z^2 x^2)_n = \frac{4}{3} \sum_n (z^4)_n.$$

We wish to relate $\sum_n (z^4)_n$ to the atomic polarizability $\alpha_a(0)$. To do this we write

$$\sum_n (z^4)_n = C \left(\sum_n (z^2)_n \right)^2.$$

For atomic hydrogen, $C = \frac{9}{2}$; using Slater orbitals we find that $C = \frac{9}{4}$ for He, and for the other rare gases it is $\frac{9}{25}$ approximately. In this approximation

$$\mu = -\frac{1}{8} \frac{\alpha_a^2(0) C \hbar \omega_a}{e Z_0^4} \frac{a}{b(\omega_a + b)}. \quad (13)$$

The polarizability is related to $\sum_n (z^2)_n$ by

$$\sum_n (z^2)_n = \frac{1}{2} \frac{\hbar \omega_a \alpha_a(0)}{e^2}. \quad (14)$$

If we take the limit in which the natural frequency of the oscillators in the dielectric solid is much greater than the excitation frequency of the atom, i. e., if $\omega_0 \gg \omega_a$, then Eq. (13) reduces to

$$\mu = -\frac{1}{8} \frac{\alpha_a^2(0)}{e Z_0^4} C \hbar \omega_a \frac{\epsilon(0) - 1}{\epsilon(0) + 1}, \quad (15)$$

as is implied by Eq. (11) and the definitions of a and b below Eq. (11). This is the form one would expect by replacing in the Hamiltonian the effect of the dielectric solid by the electrostatic image of the atom determined by classical electromagnetic theory.

If we consider the metallic limit where the plasma frequency ω_p is much greater than ω_a , then we get the same expression as given by Eq. (15) except that here $(\epsilon - 1)(\epsilon + 1)^{-1} = 1$ in view of the fact that $a = b^2$. This expression

$$\mu = -\frac{1}{8} \frac{\alpha_a^2(0) C \hbar \omega_a}{e Z_0^4} \quad (16)$$

should correspond to Antoniewicz's result. Antoniewicz calculated the induced moment for atomic hydrogen adsorbed on a metal. He obtained a dipole moment that pointed away from the surface, of magnitude $4.5 e a_0^5 Z_0^{-4}$, where a_0 is the Bohr radius. Our treatment, with $C = \frac{9}{2}$ for H, $\alpha_a(0) = 4.5 a_0^3$, and $\hbar \omega_a = \frac{1}{2} e^2 a_0^{-1}$, predicts a value of $5.7 e a_0^5 Z_0^{-4}$ [had we used $\alpha_a(0) = 4 a_0^3$, which is consistent with $\hbar \omega_a = \frac{1}{2} e^2 a_0^{-1}$, the result would have been identical with that of Antoniewicz].

If we take the other extreme in which $\omega_a \gg \omega_p$ and $\omega_a \gg \omega_0$, then formulas (15) and (16) are reduced approximately by a factor of $\omega_p/\omega_a \sqrt{2}$ or $1.1 \omega_0/\omega_a$, whichever the case may be. This extreme applies reasonably well to He on an alkali metal. Otherwise none of the extreme formulas apply to real cases.

The natural frequencies of typical dielectric solids are generally comparable to those of the atoms.

The known plasma frequencies of metals⁵ range from 3.3 eV for Cs to 25.8 eV for Au. For the case of H on Cs metal, formula (13) would give a value which is 15% of the value predicted by Eq. (16) (the electrostatic image method). For H on Au metal the corresponding reduction factor is 0.57; similar reductions would apply to other atoms.

One can also express the result in terms of the dispersion interaction energy W of the atom with the solid. Within the closure approximation we can write⁶

$$\alpha(-i\xi)/\omega_a^2 = \alpha(0)/(\omega_a^2 + \xi^2), \quad (17)$$

and obtain from Eq. (10)

$$\mu = -\frac{1}{4\pi} \frac{\alpha_a(0) C \hbar}{e Z_0^4} \int_0^\infty d\xi \alpha_a(-i\xi) \frac{\epsilon(-i\xi) - 1}{\epsilon(-i\xi) + 1}, \quad (18)$$

$$\mu = \alpha_a(0) C W / e Z_0^4, \quad (19)$$

where we have used McLachlan's formula⁷ for W .

IV. ATOM INTERACTING WITH WEAKLY COUPLED SOLID

We have also obtained an expression for μ using time-independent perturbation theory without recourse to images. This was accomplished by treating the interactions among all the atoms—both the external atom and those in the solid—on the same footing. The calculation is rather tedious and we will only give the final results. Using the Raleigh-Schrödinger wave function to third order and closure, we get

$$\mu = -\frac{\alpha_a(0) C \hbar}{2 e Z_*^4} \int_0^\infty d\xi \alpha_a(-i\xi) \left[N_0 \alpha_s(-i\xi) - \left(\frac{2\omega_0 \gamma}{\omega_a + 2\omega_0} \right) \frac{2\pi}{3} N_0^2 \alpha_s^2(-i\xi) + \dots \right], \quad (20)$$

where α_s is the polarizability of one of the isolated atoms comprising the solid; γ is a parameter which enters in averaging the inverse distance and orientation factors; Z_* is defined by

$$Z_*^4 = \frac{12}{N_0 \pi} \sum_s \frac{|Z_{as}|}{\bar{R}_{as}^3},$$

where \bar{R}_{as} is the vector between the outside atom a and an atom s of the solid, and Z_{as} is its component perpendicular to the surface.

When Z_* is large, formula (20) should correspond to the expression given by Eq. (18). To relate the series in α to the dielectric function we use a generalization of the Mazur and Mandel equation⁸ for the dielectric constant

$$\frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 1} = 2\pi N_0 \alpha(\omega) [1 - \frac{2}{3} \pi N_0 \alpha(\omega) + \mathcal{R}'], \quad (21)$$

where \mathcal{R}' corrects for the effect on the polarizabilities of the intermolecular interactions.

Using Eqs. (18), (20), and (21) gives

$$Z_0^{-4} = Z_*^{-4} \left[1 - \frac{2\pi N_0}{3} \left(1 - \frac{2\omega_0\gamma}{2\omega_0 + \omega_a} \right) \frac{\int d\xi \alpha_a(-i\xi) \alpha_s^2(-i\xi)}{\int d\xi \alpha_a(-i\xi) \alpha_s(-i\xi)} + \frac{2\pi}{3} N_0 \frac{\int d\xi \alpha_a(-i\xi) \alpha_s(-i\xi) \mathcal{R}'}{\int d\xi \alpha_a(-i\xi) \alpha_s(-i\xi)} + \dots \right]. \quad (22)$$

We estimate that in the worse case Z_0 and Z_* differ by 1%.

Only when the atom is replaced by a classical (thermal) oscillator will the Z_0 be identical with Z_* . Indeed, in this limit the atom and the solid are decoupled to all orders and the electrostatic image method is exact.

V. SUMMARY AND CONCLUSIONS

Various approximate expressions have been derived by the use of perturbation theory for the induced moment in a spherical atom near the surface of a solid. The continuum method has been used except that a discrete expression is also given for the dielectric medium of weakly coupled atoms. The validity of the results is limited by the neglect of overlap, retardation, and exchange. We find that in all cases the induced dipole moment points away from the surface.

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