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Individual atoms and molecules as dielectric media

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A clear physical connection is made between the optical response of atoms and molecules and elementary textbook discussions of the electrostatics of dielectric media. Electrons within atoms and molecules are shown to respond to the Coulomb fields of neighboring electrons in just the same way as the dipole moment of an atom responds to the fields established by dipoles on neighboring atoms. In the presence of a uniform static electric field, a nonuniform internal effective field within the electronic system can be displayed explicitly. Both screening and antiscreening of the external field are found. At finite frequency, the dielectric properties of atoms and molecules are reflected in the photoelectric cross section. The effective field at finite frequency is presented in a pictorial fashion, which helps elucidate the physics of the photoelectric emission process. Calculations of the cross section using the dielectric approach yield extremely accurate values when compared to experiment.

I. INTRODUCTION

One of the subtler topics of elementary electromagnetism is the behavior of fields in ponderable matter. Of particular import is the connection between the *macroscopic* dielectric constant and the *microscopic* polarizability. The connection usually is established in the following way.¹ Consider a dielectric crystal where virtually all the electronic charges are well localized near the constituent nuclei. In the presence of an external electric field, the charge density within each unit cell is distorted from its equilibrium configuration. The ratio of the dipole moment of the charge distortion within a given target cell to the magnitude of the external field strength from all sources is defined as the dipole polarizability α .

The macroscopic electric field which enters Maxwell's equations $\langle \mathbf{E} \rangle$ is defined as

$$\langle \mathbf{E} \rangle = \frac{1}{\Omega} \int_{\text{cell}} d\mathbf{x} \mathbf{E}(\mathbf{x}), \quad (1)$$

where $\mathbf{E}(\mathbf{x})$ is the (generally rapidly varying) microscopic field and $\Omega (= 1/N)$ is the unit cell volume; N is the number of cells. In the target cell, $\mathbf{E}(\mathbf{x})$ is divided conveniently into three parts:

$$\mathbf{E}(\mathbf{x}) = \mathbf{E}_{\text{external}}(\mathbf{x}) + \mathbf{E}_{\text{other}}(\mathbf{x}) + \mathbf{E}_{\text{self}}(\mathbf{x}). \quad (2)$$

$\mathbf{E}_{\text{external}}(\mathbf{x})$ is the field produced by charge distributions completely outside the crystal, say, from a parallel plate capacitor; $\mathbf{E}_{\text{other}}(\mathbf{x})$ is the field produced at the target cell by all other cells in the crystal; and, finally, $\mathbf{E}_{\text{self}}(\mathbf{x})$ is the field produced by the target cell's own charge distribution. Given this division, it is easy to see that the "external field" appropriate to the polarizability discussion above is defined by the relation

$$\mathbf{p} = \alpha \langle \mathbf{E}_{\text{local}} \rangle, \quad (3)$$

where

$$\langle \mathbf{E}_{\text{local}} \rangle = \langle \mathbf{E} \rangle - \langle \mathbf{E}_{\text{self}} \rangle. \quad (4)$$

The task of elementary textbook discussions is the calculation of $\langle \mathbf{E}_{\text{self}} \rangle$. From (1),

$$\begin{aligned} \langle \mathbf{E}_{\text{self}} \rangle &= \frac{1}{\Omega} \int_{\text{cell}} d\mathbf{x} \mathbf{E}_{\text{self}}(\mathbf{x}) \\ &= -\frac{1}{\Omega} \int_{\text{cell}} d\mathbf{x} \nabla \Phi_{\text{self}}(\mathbf{x}) \\ &= -\frac{1}{\Omega} \int_{\text{cell boundary}} dS \hat{n} \Phi_{\text{self}}(\mathbf{x}), \end{aligned} \quad (5)$$

where $\Phi_{\text{self}}(\mathbf{x})$ is the microscopic electrostatic potential created by the charge distribution in the target cell. This is found from Poisson's equation as

$$\Phi_{\text{self}}(\mathbf{x}) = -e \int_{\text{system}} d\mathbf{x}' \frac{\delta n(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|}, \quad (6)$$

where $\delta n(\mathbf{x})$ is the aforementioned microscopic charge distortion. The advantage of the surface integral representation $\langle \mathbf{E}_{\text{self}} \rangle$ is that (for sufficiently compact charge distributions) $\Phi_{\text{self}}(\mathbf{x})$ will be dipolar at the cell boundary. In that case, the integral is readily evaluated and one obtains the familiar Lorentz result,

$$\langle \mathbf{E}_{\text{self}} \rangle = -\frac{4\pi}{3} \frac{\mathbf{p}}{\Omega} = -\frac{4\pi}{3} \mathbf{P}, \quad (7)$$

where \mathbf{p} is the dipole moment with Cartesian components

$$p_i = -e \int_{\text{cell}} d\mathbf{x} x_i \delta n(\mathbf{x}) \quad (8)$$

and \mathbf{P} is the bulk polarization vector. Combining Eqs. (3), (4), and (7) we obtain

$$\langle \mathbf{E}_{\text{local}} \rangle = \langle \mathbf{E} \rangle + (4\pi/3)N\alpha \langle \mathbf{E}_{\text{local}} \rangle, \quad (9)$$

which self-consistently determines $\langle \mathbf{E}_{\text{local}} \rangle$:

$$\langle \mathbf{E}_{\text{local}} \rangle = \langle \mathbf{E} \rangle / [1 - (4\pi/3)N\alpha]. \quad (10)$$

The denominator includes the well-known "local field factor," which describes the influence of the environment on the target cell. Finally, from (10) and the definition of the bulk dielectric constant we obtain the Clausius-Mossotti relation

$$(\epsilon - 1)/(\epsilon + 2) = (4\pi/3)N\alpha. \quad (11)$$

Hence a macroscopic measurement of ϵ yields a value for a fundamental microscopic quantity α . This completes our review of the standard treatment of dielectrics.

Now, suppose we wish to obtain α from first principles.² From (3) and (8) we see that one needs an expression for $\delta n(\mathbf{x})$ in terms of the external perturbation $\langle \mathbf{E}_{\text{local}} \rangle$. Since the sources of $\langle \mathbf{E}_{\text{local}} \rangle$ are far from the target cell, this field is slowly varying in space. Hence $\langle \mathbf{E}_{\text{local}} \rangle \approx \mathbf{E}_{\text{local}}$, i.e., we replace a macroscopic quantity by a microscopic quantity. One can then work with the scalar potential associated with this *constant* microscopic field polarized in the j direction:

$$\Phi_{\text{local}}(\mathbf{x}) = -E_{\text{local}}x_j. \quad (12)$$

At this point one might suppose that the connection we seek between the spatially varying charge distortion $\delta n(\mathbf{x})$ and the external potential $\Phi_{\text{local}}(\mathbf{x})$ would be one of simple proportionality. Indeed, as long as the magnitude of the potential is everywhere small compared to e/a_B (true for the situations treated here), a presumed linear relationship between the two is certainly warranted. However, our general experience with charges and potentials [see, e.g., Eq. (6)] suggests that a *nonlocal* functional form may be more appropriate. Hence we are led to the very general expression

$$\delta n(\mathbf{x}) = -e \int d\mathbf{x}' R(\mathbf{x}, \mathbf{x}') \Phi_{\text{local}}(\mathbf{x}'). \quad (13)$$

In quantum theory, $R(\mathbf{x}, \mathbf{x}')$ is called the exact, microscopic density response function.³ Although the details are not crucial to us here, this function contains all of the many-body quantum mechanics of the atomic or molecular system. It is generally incalculable. Nonetheless, combining Eqs. (3), (8), (12), and (13) we obtain an exact formula:

$$\alpha_{ij} = -e^2 \int d\mathbf{x} d\mathbf{x}' x_i R(\mathbf{x}, \mathbf{x}') x'_j. \quad (14)$$

(The number of independent components of the polarizability tensor is determined by the symmetry of the unit cell constituents. The scalar notation used heretofore is appropriate for a spherically symmetric atom.) The double spatial integrations in (14) perform precisely the same type of averaging as was introduced in (1). Hence a macroscopic quantity α is obtained from a microscopic one $R(\mathbf{x}, \mathbf{x}')$.

II. MICROSCOPIC LORENTZ THEORY

In the linear response theory sketched in Sec. I, $R(\mathbf{x}, \mathbf{x}')$ is some extremely complicated functional of the exact ground state charge density of a single atom or molecule. To make progress, we must make some approximations. Suppose we are willing to neglect any effects of the Coulomb interaction beyond those accounted for by the average electrostatic Hartree potential. In that case, the effect of the external electric field can be treated by first-order perturbation theory on the occupied electron orbitals. The resulting response function $R_0(\mathbf{x}, \mathbf{x}')$ regards electrons as essentially independent entities moving in an external potential. The charge distortion then obtained from Eq. (13), $\delta n_0(\mathbf{x})$, leads immediately, using Eqs. (3) and (8), to the estimate α_0 . The quality of this *independent particle* approximation can be assessed by comparing α_0 with experimental values for a variety of systems. Table I shows that the order of magnitude obtained in this way is certainly correct, al-

Table I. Static polarizability of selected atoms and molecules for nondielectric theory and experiment.⁴ For molecules, external field is polarized along the molecular axis.

	α_0	α_{expt}	(\AA^3)
Ne	0.50	0.40	
Ar	2.6	1.64	
Xe	6.9	4.04	
N ₂	5.1	2.27	
C ₂ H ₂	27.3	4.86	

though large systematic errors remain. How might this approximation be improved?

The key point is that the charge distortion induced by $\Phi_{\text{local}}(\mathbf{x})$ is not rigid. The microscopic Coulomb potential $\Phi_{\text{self}}(\mathbf{x})$ induces further charge rearrangements within the target cell. These new distortions induce new fields, and so on. Hence $\Phi_{\text{self}}(\mathbf{x})$ is *self-consistently* determined from the two conditions

$$\delta n(\mathbf{x}) = -e \int d\mathbf{x}' R_0(\mathbf{x}, \mathbf{x}') \times [\Phi_{\text{local}}(\mathbf{x}') + \Phi_{\text{self}}(\mathbf{x}')], \quad (15a)$$

$$\Phi_{\text{self}}(\mathbf{x}) = -e \int d\mathbf{x}' \frac{\delta n(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|}. \quad (15b)$$

The essence of this "mean-field" approximation is that the density response of independent electrons to an effective field

$$\Phi_{\text{eff}}(\mathbf{x}) = \Phi_{\text{local}}(\mathbf{x}) + \Phi_{\text{self}}(\mathbf{x}) \quad (16)$$

is taken as identical to the exact density response to the local field alone [Eq. (13)]. This prescription can be rewritten as

$$\Phi_{\text{self}}(\mathbf{x}) = \Phi_{\text{self}}^0(\mathbf{x}) + e^2 \int d\mathbf{x}' d\mathbf{x}'' \times [R_0(\mathbf{x}', \mathbf{x}'') / |\mathbf{x} - \mathbf{x}'|] \Phi_{\text{self}}(\mathbf{x}''), \quad (17)$$

where $\Phi_{\text{self}}^0(\mathbf{x})$ is the Coulomb potential associated with $\delta n_0(\mathbf{x})$. The reader should note that the integral equation (17) for the microscopic field $\Phi_{\text{self}}(\mathbf{x})$ has the same structure as the algebraic equation (9) for the macroscopic field $\langle \mathbf{E}_{\text{local}} \rangle$. In particular, the kernel of the integral equation plays the role of a microscopic local field factor. Solution of Eq. (15) or (17) for $\Phi_{\text{self}}(\mathbf{x})$ and $\delta n(\mathbf{x})$ yields an improved estimate for α .

Individual atoms or molecules which comprise the bulk unit cell thus can be regarded as dielectric media in their own right. At the microscopic level, each electron responds to the fields established by the other electrons in its cell. The resulting charge distribution is characterized by a dipole moment. At the macroscopic level, each dipole responds to the fields established by dipoles from other cells. In order to obtain a deeper understanding of this fact let us look closely at some illustrative examples. We begin with a single atom.

Imagine this system subject to a long wavelength static external field polarized in the z direction such as that produced by parallel capacitor plates; this field will play the role of $\langle \mathbf{E}_{\text{local}} \rangle$ in the previous discussion. The lower panel of Fig. 1 illustrates $\mathbf{E}_{\text{eff}}(z)$, obtained as the gradient of the self-consistent potential of Eq. (16) for a typical case, xe-

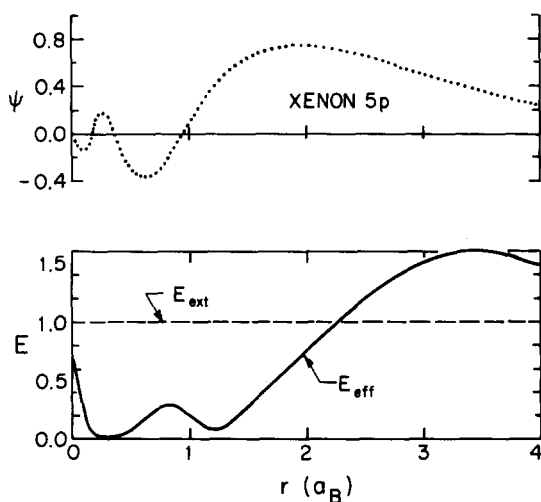


Fig. 1. Xenon 5p wavefunction (top); external and effective static fields as indicated (bottom).

non. This picture is strikingly reminiscent of the field produced in and near a macroscopic dielectric sphere, i.e., at radii greater than the sphere boundary, the total field is greater in magnitude than the external field (antiscreeing) whereas at smaller radii, the field is reduced in magnitude relative to the external field (screening). At very large radii (off the scale of Fig. 1) the two become identical. As the top panel of the figure indicates, the maximum in the outermost atomic orbital charge density can be identified as the crossover point between screening and antiscreeing of the external field. An important difference between this atom and the macroscopic dielectric sphere is that here, the field within the "sphere radius" is not uniform. Indeed, the structure observed at short distances from the nucleus correlates well with the spatial extent of interior atomic orbitals, most prominently the xenon 4d wavefunction.

A similar situation is found for molecules. In such anisotropic systems, the effective potential generally may be expanded in terms of radial functions multiplied by spherical harmonics,

$$\Phi_{\text{eff}}(\mathbf{x}) = \sum_{lm} \phi_{lm}(x) Y_{lm}(\hat{\mathbf{x}}), \quad (18)$$

with respect to the molecular center. For our example, acetylene, one finds that the induced ground state charge density is surprisingly spherical. Hence, for an external field polarized along the z axis, very little information is lost in this closed shell system by plotting (lower panel of Fig. 2) the lowest nonzero term in the sum of (18):

$$\mathbf{E}_{\text{eff}}(z) = -\frac{d}{dz} [\phi_{10}(x) Y_{10}(\hat{\mathbf{x}})]. \quad (19)$$

Once again we see that the crossover from external field enhancement to field diminution occurs at the charge density peak of the outermost wavefunction, here the acetylene $3\sigma_g$ molecular orbital. The internal structure of the effective field again correlates with a more compact polarizable orbital, the $1\pi_u$. Of particular note is the *sign reversal* of the effective field (relative to the external field) deep within the molecule. This perhaps unexpected result does not occur in textbook discussions of the macroscopic dielectric sphere and is related to our implicit use of a spatially varying microscopic dielectric function for the molecule.

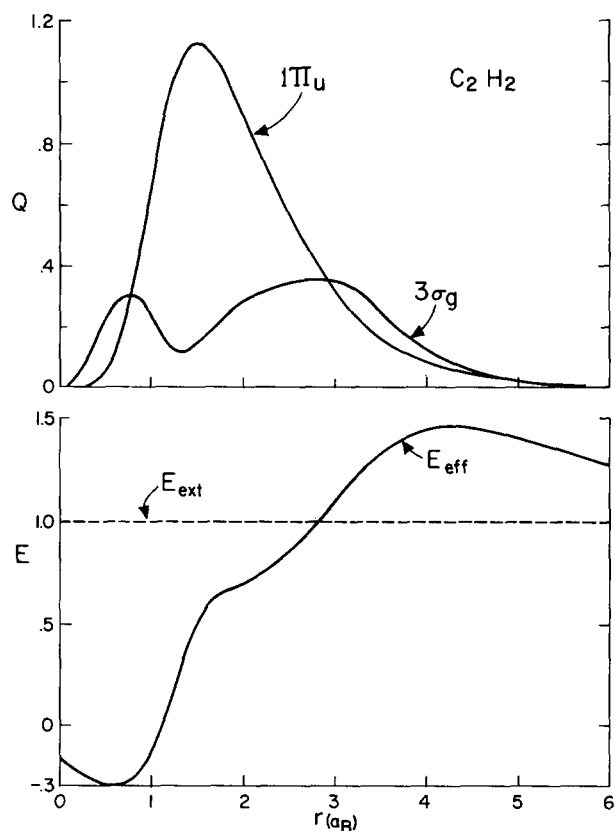


Fig. 2. Spherically averaged ground state charge densities from the $1\pi_u$ and $3\sigma_g$ levels in acetylene (top); external and effective static fields as indicated (bottom).

A comparison of Figs. 1 and 2 shows a remarkable similarity, suggesting that this form of the static screening may be characteristic of finite electronic systems in general. Indeed, Feynman has shown⁵ that the local electric field at the nucleus of an atom in an external electric field must vanish, lest the (electrically neutral) object have a net force on it.

Let us return finally to the improved estimate for $\delta n(\mathbf{x})$, and hence \mathbf{p} and α , obtained by solution of Eq. (15) or (17). Table II clearly shows that most of the discrepancy between experiment and the independent particle result is removed by properly accounting for the dielectric response of the individual atoms and molecules in just the fashion described above. Combining this type of calculation with the Clausius-Mossotti formula, i.e., performing macroscopic *and* microscopic local field theory permits accurate first-principles computation of the bulk dielectric constant ϵ .

Table II. Static polarizability of selected atoms and molecules for dielectric theory and experiment.⁴ For molecules, external field is polarized along the molecular axis.

	α	α_{expt}	(\AA^3)
Ne	0.43	0.40	
Ar	1.74	1.64	
Xe	4.12	4.04	
N ₂	2.19	2.27	
C ₂ H ₂	5.46	4.86	

When will the microscopic dielectric theory provide significant improvement over a calculation neglecting these effects? Consider the rare gas atoms. They break into two categories: He and Ne, for which the polarizability is small and both the dielectric and nondielectric theories predict the polarizability reasonably well; and Ar, Kr, and Xe, for which the polarizability is larger and the dielectric theory does a much better job than its simple rival. In the latter cases, there is a relatively low lying unoccupied d orbital to which the outermost valence (p) orbital can readily couple via *virtual* transitions. The $p \rightarrow d$ transition accounts for the majority of the polarizability. The lighter rare gases do not have a low lying d orbital; hence they are not very polarizable. (To see why low lying d orbitals only exist for the heavier rare gases, recall that in a central potential $3d$, $4d$, and $5d$ orbitals exist, whereas the $1d$ and $2d$ orbitals do not.)

Molecular nitrogen and acetylene provide another illustration of this point. Consider the polarizability along the molecular axis: It is larger in acetylene than in nitrogen. In both cases, the principal cause of screening is the virtual transitions from the occupied $1\pi_u$ orbital to the unoccupied $1\pi_g$ orbital. These matrix elements enter in the numerator of a first-order perturbation theory calculation. In the denominator, the energy difference between these two orbitals enters. However, it is only about half as great in acetylene as in nitrogen, accounting for this difference in polarizability.

The fact that the dielectric correction is most important for highly polarizable systems may be understood in terms of a simple model. Think of building up the induced charge through the summation of an infinite series. Let the first term be the charge induced by the external field, let the second term be the charge induced by the field produced by the charge of the first term, and so on. If the polarizability is small, this is a rapidly converging series, so the first term (the nondielectric theory) gives an adequate representation of the whole series. If the polarizability is large, the first term no longer approximates the whole series, so exact summation (the dielectric theory) is required. On the other hand, the nondielectric theory seems to be sufficient to predict the *relative order* of polarizabilities in a series of similar systems.

III. THE DIELECTRIC PHOTOELECTRIC EFFECT

In this section we investigate the extension of the ideas outlined above to the case of time-varying fields impinging on an atom or molecule. With no loss of generality, the time dependence of the external field may be taken to be harmonic. Thus using our previous notation,

$$\Phi_{\text{local}}(\mathbf{x}|t) = \Phi_{\text{local}}(\mathbf{x})\cos \omega t, \quad (20)$$

with $\Phi_{\text{local}}(\mathbf{x})$ given by Eq. (12). At finite frequency, electronic systems can absorb light, and if the excitation energy $\hbar\omega$ exceeds the first ionization threshold, photoelectric emission ensues. Indeed, as elementary quantum mechanics textbooks show,⁶ a quantitative measure of this phenomena is obtained as the photoelectric cross section in the familiar Fermi Golden Rule form:

$$\sigma_0(\omega) \sim \sum_{i,f} |\langle f | \Phi_{\text{local}}(\mathbf{x}) | i \rangle|^2 \delta(\hbar\omega - E_f + E_i). \quad (21)$$

In the present context, we wish to know if dielectric effects play a significant role in first-principles calculations

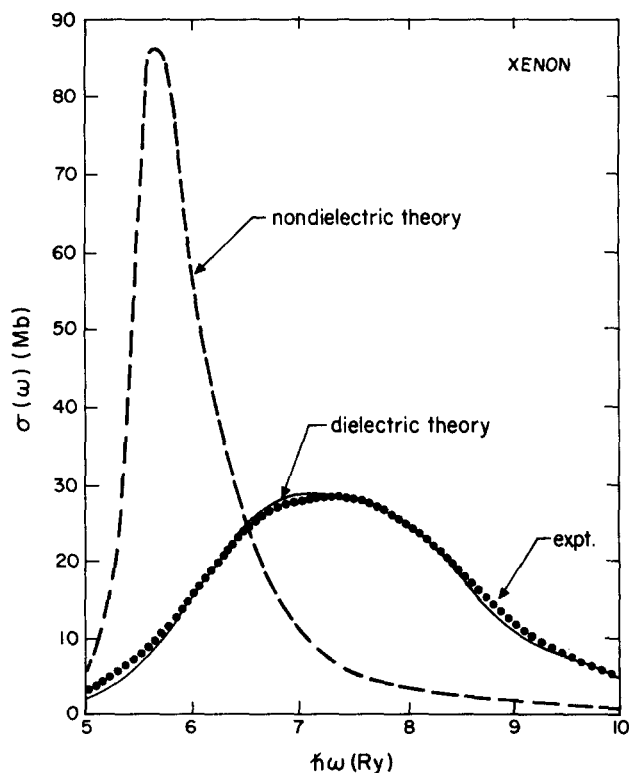


Fig. 3. Photoemission cross section versus photon energy for xenon; theory and experiment⁷ as indicated.

of photo-cross sections. The subscript on the left-hand side of (21) is meant to indicate that the standard formula is precisely analogous to what was called the independent particle approximation in Sec. II. We test its efficacy here, as before, by direct comparison to experiment. The dashed curve in Fig. 3 illustrates the result of evaluating the Golden Rule expression using initial and final state atomic wavefunctions for xenon at excitation energies around 100 eV. The dotted curve shows the absolute experimental data obtained using a synchrotron radiation source.⁷ The lack of agreement is quite striking.

Our dielectric theory approach to correcting the discrepancies is a straightforward generalization of the methodology of Sec. II. For a time-dependent external perturbation, we focus on the Fourier frequency components of the charge distortion induced by the external field. The independent particle approximation reads

$$\delta n(\mathbf{x}|\omega) = -e \int d\mathbf{x}' R_0(\mathbf{x}, \mathbf{x}'|\omega) \Phi_{\text{local}}(\mathbf{x}'), \quad (22)$$

where the frequency-dependent response function $R_0(\mathbf{x}, \mathbf{x}'|\omega)$ now is obtained by first-order *time-dependent* perturbation theory. At the frequencies of interest, $\delta n(\mathbf{x}|\omega)$ is a complex number. This simply means that the charge distortion may oscillate out of phase with respect to the external field. Precisely as before, we can think in terms of the induced Coulomb fields, again complex numbers, which drive further distortions of the charge density. In fact, we can write down immediately the time-dependent analog to Eq. (17) which solves the problem self-consistently:

$$\Phi_{\text{eff}}(\mathbf{x}|\omega) = \Phi_{\text{local}}(\mathbf{x}) + e^2 \int d\mathbf{x}' d\mathbf{x}'' \times [R_0(\mathbf{x}', \mathbf{x}''|\omega)/|\mathbf{x} - \mathbf{x}'|] \Phi_{\text{eff}}(\mathbf{x}''|\omega). \quad (23)$$

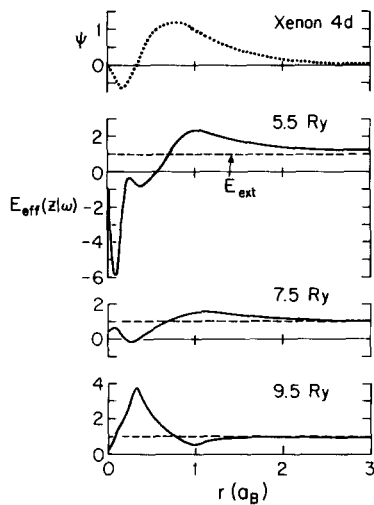


Fig. 4. Xenon 4d wavefunction (top); real part of effective field (—) and external field (---) for three photon energies (bottom three panels).

[Actually, this is an equation for the total effective field rather than Φ_{self} ; the connection is seen in Eq. (16).] Note that the effective potential acquires an *additional* frequency dependence in addition to the harmonic dependence, viz.,

$$\Phi_{\text{eff}}(\mathbf{x}|t) = \text{Re}[\Phi_{\text{eff}}(\mathbf{x}|\omega)] \cos \omega t + \text{Im}[\Phi_{\text{eff}}(\mathbf{x}|\omega)] \sin \omega t. \quad (24)$$

The complex notation implies only that the effective field is, in general, out of phase with the driving field $\Phi_{\text{local}}(\mathbf{x})$. The appropriate prescription for calculation of the observables is simply to *replace* $\Phi_{\text{local}}(\mathbf{x})$ by $\Phi_{\text{eff}}(\mathbf{x}|t)$ in the Golden Rule:

$$\sigma(\omega) = \sum_{if} |\langle f | \Phi_{\text{eff}}(\mathbf{x}|\omega) | i \rangle|^2 \delta(\hbar\omega - E_f + E_i). \quad (25)$$

The solid curve in Fig. 3 illustrates the result obtained for the cross section of xenon according to this dielectric theory. In this case, and in many others, remarkably good agreement with experiment is found simply by extending the ideas of classical dielectric theory to the atomic regime.

A clear physical picture of the photoabsorption/photoemission process in the frequency interval of Fig. 3 is obtained by appeal to the pictorial representation. Figure 4 illustrates $E_{\text{eff}}(z|\omega)$ at three frequencies which span the range of Fig. 3. [To facilitate comparison with the constant external field only the real part of $E_{\text{eff}}(z|\omega)$ is shown.] The 5.5 Rydberg panel is quite similar to the zero-frequency result of Sec. II. Both screening and antiscreening occur with significant variations in both the magnitude and direction of the effective field as one traverses the atom. Note that the dielectric sphere “radius” now coincides with the charge density maximum of the xenon 4d shell. The physics of this is simply that the excitation frequency is quite near the 4d ionization energy and this shell is thereby most strongly coupled to the external perturbation.

In fact, an analogy which regards the entire 4d shell as a damped, driven harmonic oscillator is quite apt. Let us take the orbital induced charge density as the natural oscillator coordinate. In this simple model, the cross-section curve labeled “nondielectric theory” in Fig. 3 would be obtained

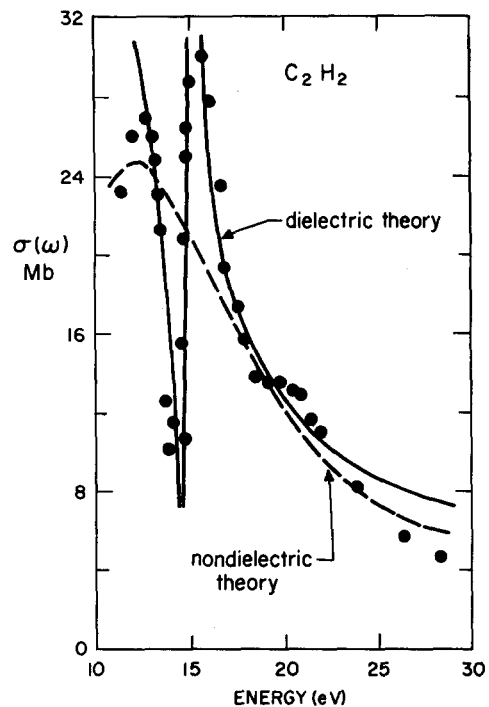


Fig. 5. Photoemission cross section versus photon energy for acetylene. Theory as indicated; experiment from Ref. 8.

from the solution to

$$\delta \ddot{n} + \gamma \delta \dot{n} + \omega_0^2 \delta n = E_{\text{local}} \cos \omega t. \quad (26)$$

Here, $\omega_0 \approx 5.5 \text{ Ry}$ and $\gamma \approx 1 \text{ Ry}$. The dielectric theory curve results when one notices that the right-hand side of Eq. (26) should include the additional term $E_{\text{self}}(\omega) \cos \omega t$. But $E_{\text{self}}(\omega)$ itself depends linearly on the induced density [cf. Eq. (6)]. Therefore, since $E_{\text{self}}(\omega)$ is complex, both the oscillator frequency *and* the damping constant are renormalized.

We return to the molecular example C_2H_2 in Fig. 5. Again, the dashed curve shows the Golden Rule result when dielectric effects are neglected and the dots denote experimental points.⁸ The very sharp resonance structure observed in the data is due to interference between two degenerate competing excitation channels. On one hand, direct photoelectric emission from the outermost $1\pi_u$ molecular orbital can readily occur for energies above 11.4 eV.⁹ On the other hand, very near 14 eV, discrete line absorption can occur between the occupied $2\sigma_u$ level and the unoccupied, yet bound, $1\pi_g$ orbital. If one imagines these processes as each creating elementary dipolar charge distortions, it is clear that there will be a dipole-dipole interaction between them.

The dielectric theory propounded here includes this effect. The solid curve in Fig. 5 shows that quite good agreement with experiment is obtained. In the language we have used previously, a resonantly large amount of charge builds up when external fields near the transition frequency are applied. This charge distribution gives rise to a large induced field with a strong frequency dependence. Figure 6 shows the variation of the real part of the total field (to be compared with $E_{\text{ext}} = 1$ everywhere) and its imaginary part (to be compared with a 90° out-of-phase component of zero in the usual description). The external field is polarized

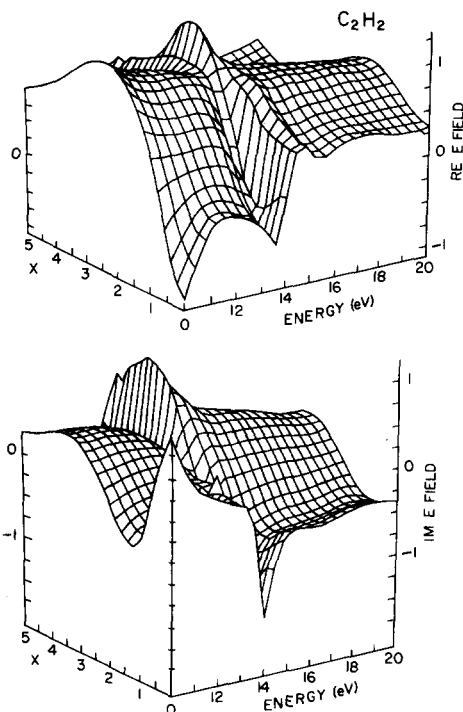


Fig. 6. Effective field for acetylene perpendicular to the molecular axis for an external field polarized in this direction for a range of photon energies. Real part (top); imaginary part (bottom).

along the axis of the linear C_2H_2 system and the figure shows the spatial dependence along an axis (labeled X) perpendicular to the molecular axis and passing through the center of the molecule. The resonant behavior near 14 eV is quite marked. By careful examination of the fields one can understand the variations of the cross section in some detail. Even if this is not done, Fig. 6 is meant to indicate, in a qualitative way, the magnitude and complexity of dielectric effects in seemingly simple electronic systems.

IV. CONCLUSION

The purpose of this work was to provide a simple means to visualize rather complex many-electron effects in the interaction of radiation with matter using ideas familiar

from classical electromagnetic dielectric theory. Details of the explicit calculations have been omitted intentionally in order to emphasize the simplicity of the dielectric interpretation.¹⁰ In short, electrons within an atom or molecule behave quite similarly to dipoles in ponderable matter. A relatively simple formalism not only brings theory and experiment into good agreement (for dipole polarizabilities and photoelectric cross sections) but allows for a pictorial description of microscopic screening. It may amuse the reader to imagine the extension of these notions to other optical phenomena.

ACKNOWLEDGMENTS

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¹E. M. Purcell, *Electricity and Magnetism* (McGraw-Hill, New York, 1965), Chap. 9; see, also, D. E. Aspnes, *Am. J. Phys.* **50**, 704 (1982).

²The general approach taken here is well known in the literature of solid-state physics. See, for example, N. Wiser, *Phys. Rev.* **129**, 62 (1963). The formalism was made explicit for atoms and molecules by W. Brandt and S. Lundqvist, *Ark. Fys.* **28**, 399 (1965).

³See, for example, D. Pines and P. Nozieres, *The Theory of Quantum Liquids* (Benjamin, New York, 1966), Chap. 2.

⁴Atomic values from T. M. Miller and B. Bederson in *Advances in Atomic and Molecular Physics*, edited by D. R. Bates and B. Bederson (Academic, New York, 1977), Vol. 13. Molecular values from G. R. Alms, A. K. Burnham, and W. Flygare, *J. Chem. Phys.* **63**, 3321 (1975).

⁵R. P. Feynman, *Phys. Rev.* **56**, 340 (1939).

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SOLUTION TO THE PROBLEM ON PAGE 1141

If the hole is drilled at a height h above the ground then the velocity of the water is given by

$$v^2 = 2g'(H - h), \quad (1)$$

where $g' = g/(1 - r^4/R^4)$.

The trajectory of the water is a parabola. When the water hits the ground, $y = 0$ and $x = R$, where R is the range. Hence,

$$[1 + \tan^2(\theta)]R^2 = (2v^2/g')[\tan(\theta)R + h] \quad (2)$$

where θ is the angle of elevation of the nozzle.

For a fixed value of h the maximum range is obtained by setting $dR/d\theta = 0$.

One obtains

$$\tan(\theta) = v^2/g'R, \quad (3)$$

Then

$$R^2 = 4H(H - h). \quad (4)$$

R has its largest value, $R_{\max} = 2H$, for $h = 0$.

The solution is independent of the size of the tank and the size of the hole.

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