with coupling V_0 and coupled to the $M = \pm 1$ components with coupling V_1, then it was found that the only modification from the singlet-singlet results presented here was the replacement $V \to (V_1^2 + V_2^2)^{1/2}$.

[16]W. A. Little and H. Gutfreund, Phys. Rev. B **4**, 817 (1971).

[17]K. Mees, *The Theory of the Photographic Process* (MacMillan, New York, 1942), p. 1002.

Local-Field Effects in the Optical Properties of Solids: The Far-Ultraviolet Spectra of Ionic Crystals

T. K. Bergstresser*

Department of Physics, University of Wisconsin, Madison, Wisconsin 53706

and

G. W. Rubloff†

Department of Physics, Brown University, Providence, Rhode Island 02912
(Received 26 December 1972)

We consider a case, the far-ultraviolet spectrum of an ionic crystal, where the local-field effects on the optical properties can easily be understood. The results show how local-field effects modify the optical properties of solids and complicate their interpretation and comparison with theory.

Theoretical calculations of the optical properties of solids usually assume that electronic transitions are caused by the average electric field produced by the applied field of the photon plus the spatially averaged field due to the response of the medium. However, the induced polarization of the medium is nonuniform, so that spatially varying microscopic fields are generated which differ locally from the average field. These "local-field effects" give rise to a difference between the measured dielectric response ϵ and the dielectric function $\tilde{\epsilon}$ calculated using the above assumption. These effects have long been taken into account in their region of obvious applicability, such as a localized impurity state in an insulator for frequencies below the band gap,[1] but local-field effects in the fundamental absorption region have rarely been treated.[2-4]

We present a case where local-field effects on the optical properties of a solid can easily be taken into account. This is timely because of the vast increase in experimental data in the uv and soft–x-ray region, where the local-field effects are most influential. When large, they change and complicate the relation between measured optical properties and electronic band structure, so it is important to understand their influence. To expose the difference between ϵ and $\tilde{\epsilon}$, we compare the experimental ϵ not to an actual calculation, which may contain errors, but to an inferred $\tilde{\epsilon}$ which would be obtained from

a calculation accurate in all respects except for neglect of local-field corrections. The inferred $\tilde{\epsilon}$ comes from a simple model for the local-field effects. In addition, the results indicate how local-field effects may influence the qualitative behavior of the optical spectra of solids in which the model is less appropriate for quantitative predictions.

A simple model for local-field effects is the classical Lorentz local field,[5] which applies to a cubic lattice of polarizable particles small compared to the lattice constant. This picture leads to the Lorentz-Lorenz relation, which can be written in terms of the real and imaginary parts (subscripts 1 and 2) of the dielectric function

$$\epsilon_1(\omega) = 1 + \frac{\tilde{\epsilon}_1 - 1 - \frac{1}{3}[(\tilde{\epsilon}_1 - 1)^2 + \tilde{\epsilon}_2^2]}{[1 - \frac{1}{3}(\tilde{\epsilon}_1 - 1)]^2 + \frac{1}{9}\tilde{\epsilon}_2^2}, \tag{1a}$$

$$\epsilon_2(\omega) = \frac{\tilde{\epsilon}_2}{[1 - \frac{1}{3}(\tilde{\epsilon}_1 - 1)]^2 + \frac{1}{9}\tilde{\epsilon}_2^2}. \tag{1b}$$

We expect the Lorentz local-field model to apply to the far-uv spectra of ionic crystals because the initial states, particularly the core states, are strongly localized. We consider here the optical spectrum of CsCl at 90°K, which exhibits relatively strong local-field corrections. Its reflectance spectrum has been measured by one of us[6] in the range 6–26 eV using synchroton radiation from the Physical Science Laboratory elec-

tron storage ring at the University of Wisconsin. By standard Kramers-Kronig analysis of this data we have obtained the dielectric function $\epsilon(\omega)$, shown by the solid curves in Fig. 1. The structures between 7 and 13 eV arise from excitations of the spin-orbit–split valence bands, while above 13 eV the features are caused primarily by excitation of the spin-orbit–split $Cs^+(5p)$ core level. In both regions, the sharp, lower-lying transitions are excitonic in nature.

The dashed curves in Fig. 1 show the dielectric function $\tilde{\epsilon}$ related to ϵ by Eq. (1). The differences between ϵ and $\tilde{\epsilon}$ illustrate the effects of local-field corrections on the optical properties. We concentrate our attention on the rather striking changes which occur in going from $\tilde{\epsilon}_2$ to ϵ_2: (1) Relative peak heights are altered; (2) structures shift to lower energy; (3) the shapes of structures (particularly the asymmetric peaks, e.g., at 8.7

and 16.5 eV) change; and (4) $\tilde{\epsilon}_2 < \epsilon_2$ at lower energy, whereas at higher energies the opposite is true. These effects are more easily understood if $\tilde{\epsilon}$ is a simple function of ω. If $\tilde{\epsilon}$ is composed of a single Lorentzian structure, ϵ is also a Lorentzian, but the center frequency ω_0 is shifted downward by an amount related to the oscillator strength. If $\tilde{\epsilon}$ is a Lorentzian peak superposed on a smooth background, then the peak in ϵ can undergo an apparent change in oscillator strength, and an asymmetry similar in appearance to an antiresonance can develop, but the dip can occur only on the high-frequency side. Two neighboring peaks in $\tilde{\epsilon}$ will undergo an altering of shape. When $\tilde{\epsilon}$ obeys the usual requirements of a dielectric function, and when $\tilde{\epsilon}$ is analytic in the upper half ω plane [and if $\epsilon(0) - 1 < 3$, the condition for avoidance of the static dielectric catastrophe], then $\epsilon(\omega)$ is also analytic in the
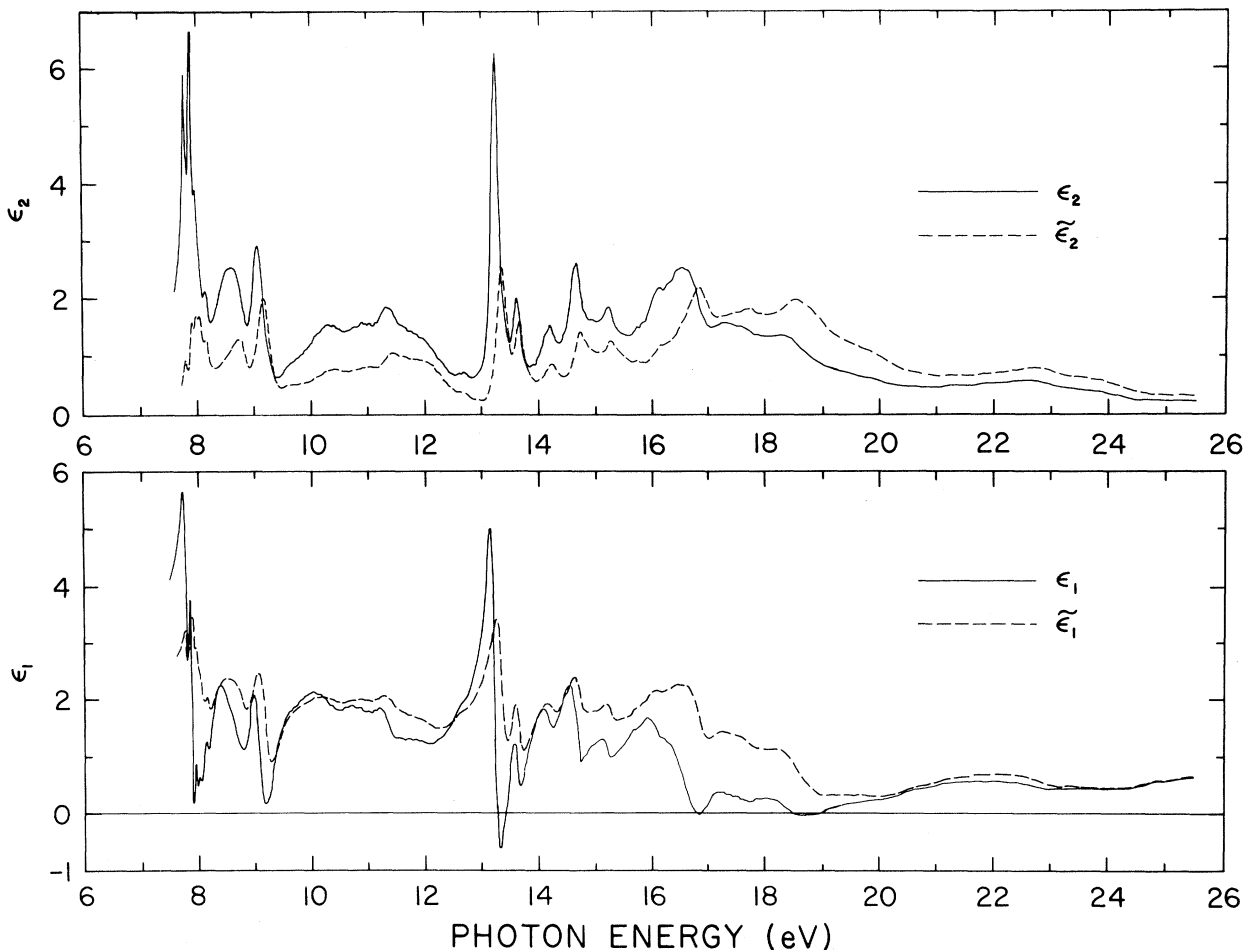

FIG. 1. Local-field effects on the imaginary (ϵ_2) and real (ϵ_1) parts of the dielectric function of CsCl in the far ultraviolet at 90°K. Solid curves are experimental, determined by Kramers-Kronig analysis of reflectance data. Dashed curves, dielectric function corresponding to ϵ in the absence of local-field effects.

upper half ω plane. In addition,

$$\int_0^\infty \omega \epsilon_2(\omega)\, d\omega = \int_0^\infty \omega \tilde{\epsilon}_2(\omega)\, d\omega,$$

so that the total oscillator strength is preserved. The data in Fig. 1 give for the effective number of electrons $n_{\text{eff}} = 11.2$ at 25 eV and 16.4 at 50 eV, while $\tilde{n}_{\text{eff}} = 9.7$ at 25 eV and 15.8 at 50 eV.

The Lorentz local-field model, which leads to Eq. (2), applies if the electric-dipole transition moment is composed of nonoverlapping, spherically-symmetric distributions centered at the cubic lattice sites. Assuming this distribution is equivalent to making the dipole approximation of Ref. 2. In this case the field perturbing states centered at a site, when averaged over a sphere centered at the site, is the Lorentz local field. The deviation from strict spherical symmetry of the transition moment is not a serious concern, but it is crucial to assume that moments from neighboring sites do not overlap. This approximation is good for core states. Because the valence bands in ionic crystals such as CsCl are rather narrow (~ 0.75 eV wide[6]), the bulk of the charge density is spherically symmetric and localized, so that the approximation retains a measure of validity here, too. The final states are involved in the dipole transition moment in a way symmetric with the initial states, but the behavior of the moment for transitions which are not weak is dominated by the more localized initial state. Transitions to excitonic final states involve only slightly more localized transition moments and do not produce local-field effects significantly different from those for ordinary interband transitions. Finally, we note that the Lorentz local-field model requires $|ka|^2 \ll 1$, where k is the wave vector of the photon in the solid, and a is the lattice constant.

Significant local-field effects qualitatively similar to those shown in Fig. 1 will occur if the initial states being excited are strongly localized and also $|\tilde{\epsilon}_1 - 1|$ and $\tilde{\epsilon}_2$ are not both small compared to 1, i.e., roughly the photon energy range 10 to 100 eV. For lesser degrees of localization the local-field effects are correspondingly weaker. For example, the corrections to the valence-band excitation spectra in Fig. 1 are somewhat exaggerated because the valence bands are less localized than the core bands. On the other hand, if the transition moment is roughly constant over the unit cell, as in valence-band excitations of simple metals, then $\epsilon = \tilde{\epsilon}$.

The results described here have significant implications, for they provide a qualitative picture,

and in some cases a quantitative estimate, of the influence of local-field effects. For example, consider the relation between computed ($\tilde{\epsilon}$) and measured (ϵ) dielectric functions for the sequence of semiconductors Ge, GaAs, ZnSe, MgO, and NaCl.[7] They are ordered by increasing ionicity, but the valence-band states of even the less ionic materials have by no means an approximately uniform charge density over the unit cell.[8] Thus the local-field effects discussed here should be present to some extent in these materials. The model, Eq. (1), for estimating the effects will be more accurate further along the sequence, where the localization of the valence-band states is stronger. It has been found that, particularly for the more ionic substances, the measured ϵ_2 has more oscillator strength at low frequencies than does the calculated $\tilde{\epsilon}_2$, whereas $\epsilon_2 < \tilde{\epsilon}_2$ at higher frequencies. As we have shown, consideration of local-field corrections will reduce this disparity. Exciton effects, i.e., the final-state interaction between the electron and the hole frequently neglected in calculations of the dielectric function, are also important in explaining the disagreement between ϵ and $\tilde{\epsilon}$, but it appears that the entire discrepancy should not be ascribed to them. These two distinct effects can both be important for ϵ.

Local-field effects can complicate the interpretation of other influences on the optical spectra. For example, (1) the observed intensity ratio of spin-orbit–split exciton peaks, taken as a measure of their oscillator strength, has been used to estimate the exchange interaction between electron and hole.[9,10] These estimates may be incorrect because local-field effects can influence the apparent oscillator strength (cf. Fig. 1.). (2) Antiresonances observed in the exciton line shapes of semiconductors and insulators have been attributed[11] to interference[12] between the exciton and interband continuum states of the electron and hole. Local-field effects can also produce an antiresonance-like dip on the high-energy side of a peak in ϵ_2, complicating the interpretation of the interference-induced antiresonance, which can give a dip on either side.

A more fundamental approach capable of describing local-field effects for cases intermediate between Eq. (1) and $\epsilon = \tilde{\epsilon}$ has been attempted by Van Vechten and Martin.[3a] They used the dielectric matrix $\epsilon_{GG'}(q, \omega)$ to calculate the microscopic polarization fields in diamond and the consequent ϵ^{micro} which includes local-field corrections to $\tilde{\epsilon}$. However, they neglected to subtract

from the total microscopic field the self-field of the electron being excited, which does not contribute to the local field inducing the transition. As a result, they found $\epsilon_2^{micro} < \tilde{\epsilon}_2$ for lower ω, increasing the disparity between theory and experiment, which is to be expected. In fact, subtracting the self-field will enhance ϵ_2^{micro} over $\tilde{\epsilon}_2$ for lower ω and bring about closer agreement between theory and experiment. This is a result of the transformation in Eq. (1), as seen in Fig. 1, and even when there are ions at noncubic sites, we find $\epsilon_2^{micro} < \epsilon_2$ for low ω. Thus their hypothesis of significant dynamical correlation effects is unnecessary. Subtraction of the electron's self-field, a difficult problem, might be best accomplished by use of a phenomenological parameter, as suggested by Wiser.[2]

In summary, the influences of local-field effects in the optical spectra of solids must be kept in mind when the spectra are interpreted or used to evaluate theoretical calculations. An upper limit to the magnitude of local-field corrections is obtained from Eq. (1), while the degree of initial-state localization suggests what fraction of the full Lorentz local-field correction is appropriate.

We appreciate the encouragement and support of Professor H. Fritzsche.

[1]See, e.g., F. Stern, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1963), Vol. 15, Sect. 24.

[2]N. Wiser, Phys. Rev. 129, 62 (1963); S. L. Adler, Phys. Rev. 126, 413 (1962).

[3a]J. A. Van Vechten and R. M. Martin, Phys. Rev. Lett. 28, 446 (1972).

[3b]R. M. Martin *et al.*, Phys. Rev. B 6, 2500 (1972).

[4]M. A. Graber, thesis, Princeton University, 1970 (unpublished).

[5]See, e.g., J. M. Ziman, *Principles of the Theory of Solids* (Cambridge Univ. Press, London, 1964), p. 229.

[6]G. W. Rubloff, Phys. Rev. B 5, 662 (1972).

[7]M. L. Cohen and V. Heine, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1970), Vol. 24, and references therein.

[8]J. P. Walter and M. L. Cohen, Phys. Rev. B 4, 1877 (1971).

[9]Y. Onodera and Y. Toyozawa, J. Phys. Soc. Jap. 22, 833 (1967).

[10]H. Saito, Sci. Light (Tokyo) 20, 1 (1971).

[11]J. C. Phillips, Phys. Rev. Lett. 12, 447 (1964); K. P. Jain, Phys. Rev. 139, A544 (1965).

[12]U. Fano, Phys. Rev. 124, 1866 (1961).

Random-Phase-Approximation Correlation Energy in Metallic Hydrogen Using Hartree-Fock Bloch Functions*

Hendrik J. Monkhorst and Jens Oddershede†
Department of Physics, University of Utah, Salt Lake City, Utah 84112
(Received 22 January 1973)

Correlation energies for simple-cubic metallic hydrogen are calculated using random-phase-approximation (RPA) methods. Hartree-Fock Bloch functions for the real lattice, including those for excited bands, were used as zeroth-order states. About 60% of the RPA correlation energy originates from intraband excitations. The RPA correlation energy, including exchange, is estimated to be about -0.024 hartree/electron near the Hartree-Fock equilibrium, leading to a total energy of about -0.490 hartree/atom.

The treatment of electron correlation effects in real metals is still an outstanding problem. For the limiting cases of high and low electron densities satisfactory methods exist.[1,2] The difficulties at intermediate densities arise since the kinetic energy and potential energy are comparable. This leads to the breakdown of the electron-gas model, particularly for the calculation of total energies, since the actual electron-lattice interactions are not negligible. But this implies that plane waves are no longer appropriate unperturbed functions in a perturbation treatment of the correlation problem. In this communication we present many-body theoretical results of correlation-energy calculations for simple-cubic metallic hydrogen using Hartree-Fock Bloch