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New model dielectric function and exchange-correlation potential for semiconductors and insulators

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We propose a new model frequency and wave-vector-dependent dielectric function for systems with an energy gap in their electronic excitation spectrum. The function is homogeneous, isotropic, and causal and satisfies two sum rules relating to particle-number conservation. Moreover, it has an analytic representation, reduces to the Lindhard function in the limit of zero gap, and compares well numerically with the $\epsilon(q,\omega)$ of Si from band-structure calculations. With the model irreducible polarizability, we extend the theory of Singwi *et al.* [Phys. Rev. B 1, 1044 (1970)] to obtain a one-parameter family of exchange-correlation potentials appropriate for semiconductors and insulators. The existence of a band gap is found to enhance the exchange contributions but reduces the correlation contributions to the exchange-correlation potentials resulting in an overall potential which deepens as the average band gap of the system increases. A band calculation of silicon in the present theory shows a slight improvement of the band gaps over previous work using the metallic exchange-correlation potential.

I. INTRODUCTION AND SUMMARY

The theorems of Hohenberg and Kohn,[1] and Kohn and Sham[2] guarantee the existence of a unique electron density functional with which the ground-state exchange and correlation energy of any system can be found. Unfortunately, their proof is not constructive, and the functional remains unknown. In most practical electronic-structure calculations, the density functional is approximated by a local functional, namely, with the exchange-correlation energy density replaced by that of an electron gas with the same local density. There have been attempts to go beyond the local-density approximation, for example, the gradient expansion[1,2] and the weighted density approximation.[3] The former approach has not met with great success, and the latter has yet to be tested for band-structure calculations. There is no guarantee of uniqueness or correctness for the exchange-correlation functional derived from electron-gas data when applied to another system.

In the theory of Singwi and co-workers[4,5] (SSTL), the electron-gas exchange-correlation potential is tied intimately to its electronic excitation spectrum through the irreducible polarizability and the corresponding dielectric (Lindhard) function.[6] This electron-gas local-density functional has been applied to metals and insulators alike, even though their excitation spectra are quite different. In the present work, we propose a new model dielectric function which allows for the possibility of a gap in the electronic excitation spectrum. The irreducible polarizability associated with the model dielectric function is then used in the formulation of SSTL to find an exchange-correlation potential for semiconductors and insulators. The new potential thus preserves the simplicity of a local-density theory while incorporating an important feature of the real systems in an approximate way.

The important parameter in the model dielectric function and, hence, in the exchange-correlation potential is $\lambda = E_g/E_F$ where E_g is the average band gap and E_F is the Fermi energy. We find that, upon the introduction of a finite λ, the exchange part of the exchange-correlation potential is enhanced but the correlation part reduces slightly. The overall result is an attractive potential which deepens as λ increases. In a specific application of the new potential to Si (with $\lambda = 0.4$), the various band gaps are found to be slightly wider (in closer agreement with experiment) than the values obtained from calculations using a potential extracted from the electron-gas data. We expect this to be a general result arising from the deeper exchange-correlation potential at the bond sites which would lower the valence-band-state energies more than the conduction-band-state energies.

The remainder of the paper is organized as follows: In Sec. II, we briefly review the electron-gas theory. In Sec. III, the model dielectric function is presented. In Sec. IV, we discuss the exchange and correlation effects associated with this model system, including an explicit exchange-correlation potential. Finally, in Sec. V, the new potential is applied to the calculation of the band structure of Si.

II. ELECTRON-GAS THEORY OF SSTL

There have been many calculations of the ground-state properties of the electron gas. Hedin and Lundqvist[7] have reviewed this work up to 1971. Gorobchenko and Maksimov[8] have presented a more recent review. The work of Singwi and co-workers[4,5] has, however, remained a standard, convenient approach for the derivation of an exchange-correlation potential for electronic-structure calculations of real materials.

In this section, we briefly review the formulation of Singwi and co-workers. In both papers,[4,5] the dielectric function $\epsilon(q,\omega)$ and the static structure factor $S(q)$ are determined self-consistently. The structure factor is related to the pair correlation function $g(r)$ by

$$1-g(r)=\frac{3}{2q_F^3 r}\int_0^\infty q\sin(qr)[1-S(q)]dq\ , \tag{2.1}$$

where q_F is the Fermi wave vector of free particles of given density, and r is the distance from a given electron to a point in the electron gas. The exchange-correlation hole about any point is thus described in real space by $1-g(r)$ and in transform space $1-S(q)$ with $S(q)$ given by

$$S(q)=-\frac{\hbar q^2}{4\pi^2 e^2 n}\int_0^\infty \mathrm{Im}\left[\frac{1}{\epsilon(q,\omega)}\right]d\omega\ , \tag{2.2}$$

where n is the number density of electrons.

In obtaining the exchange-correlation energy of an electron gas, the scheme of SSTL consists of solving Eq. (2.2) along with the approximate expression

$$\epsilon(q,\omega)=1+\frac{Q_0(q,\omega)}{1-G(q)Q_0(q,\omega)}\ , \tag{2.3}$$

where

$$G(q)=\frac{1}{n}\int\frac{\vec{q}\cdot\vec{q}\,'}{q'^2}\frac{[1-S(\vec{q}-\vec{q}\,')]}{\epsilon(q')}\frac{d^3q'}{(2\pi)^3} \tag{2.4}$$

and $-q^2Q_0/4\pi e^2$ is the free-electron polarizability. [In Ref. 4, $\epsilon(q')$ is omitted in Eq. (2.4).] The interaction energy per particle (Coulomb energy associated with the exchange-correlation hole) is evaluated from

$$E_{\mathrm{int}}(e^2,r_s)=\frac{1}{2}\int\frac{4\pi e^2}{q^2}[S(q)-1]d^3q\ , \tag{2.5}$$

where r_s is the electron-gas parameter. The exchange-correlation energy per particle is found via the relations

$$\begin{aligned}E_{\mathrm{xc}}(\xi,r_s)&=\int_0^\xi\frac{\partial E_{\mathrm{xc}}(\xi',r_s)}{\partial\xi'}d\xi'\\&=\int_0^\xi E_{\mathrm{int}}(\xi',r_s)\frac{d\xi'}{\xi'}\ .\end{aligned} \tag{2.6}$$

Finally, the exchange-correlation potential which is the functional derivative of the total exchange-correlation energy is given by

$$V_{\mathrm{xc}}=\frac{\delta(\rho(\vec{r})E_{\mathrm{xc}}[\rho(\vec{r})])}{\delta\rho(\vec{r})}\ , \tag{2.7}$$

where $E_{\mathrm{xc}}[\rho(\vec{r})]$ is the exchange-correlation energy per particle for the charge distribution $\rho(r)$. The fundamental input in obtaining a metallic V_{xc} in this scheme is the use of the Lindhard Q_0 in Eq. (2.3).

III. MODEL DIELECTRIC FUNCTION

The exact many-body dielectric function gives a detailed description of a system including both ground-state and excited-state properties.[9] Formulas for the dielectric function of a crystal in the self-consistent-field approximation (or random-phase approximation) have been known for some time.[10-12] However, due to the large scale of the computation involved, there are only a few self-consistent-field calculations of the dielectric function for real materials.[13-15] Calculations beyond the self-consistent-field approximation[16] are even more rare.

Model dielectric functions have been introduced as a practical simplification. For metals, the electron gas serves as a model system. In particular, the dielectric function in the self-consistent-field approximation was found analytically by Lindhard.[6] Unfortunately, there is no correspondingly attractive model for semiconductors and insulators. Penn[17] proposed one model for a semiconductor by extending the nearly-free-electron model isotropically in three dimensions. The Penn model dielectric function[17–19] gives a reasonable description of the static screening properties of semiconductors. There are some frequency and wave-number-dependent model dielectric functions. Milchev[20] has proposed one and compiled references to several others. These models are often derived with *ad hoc* assumptions. Important sum rules may be violated. Some are extremely simplified such as the plasmon-pole model[21] where the plasmon and the particle-hole excitations are approximated simply with a plasmon contribution.

In this work, we propose a new model dielectric function with both frequency and wave-vector dependence. While we offer no derivation as in some previous models, we will show that the new model function has many desirable features including causality (through the Kramers-Krönig relations), particle-number conservation (through two sum rules), homogeneity, isotropy, and an analytic representation. The imaginary part of the new model dielectric function is defined by

$$\epsilon_2(q,\omega)=\begin{cases}\epsilon_2^L(q,\omega_-), & |\omega|\geq\lambda\omega_F\\ 0, & |\omega|<\lambda\omega_F\end{cases} \tag{3.1}$$

where $\omega_F=E_F/\hbar$, $\omega_-^2=\omega^2-(\lambda\omega_F)^2$ with the sign of ω_- taken to be the same as the sign for ω, and ϵ^L is the Lindhard dielectric function. This is a two-parameter model. In addition to the electron-gas parameter r_s, the lowest excitation frequency (or "gap") is given by $\lambda\omega_F=E_{g/\hbar}$. Obviously, if $\lambda=0$, the model function reduces to the Lindhard function.

For the new function, we may immediately derive the f-sum rule

$$\int_0^\infty \epsilon_2(q,\omega)\omega\, d\omega=\tfrac{1}{2}\pi\omega_p^2 \tag{3.2}$$

by a change of variables and reference to the corresponding property of the Lindhard function. The Kramers-Krönig relation generates the real part of the model dielectric function. By a similar change of variables, we obtain the result for frequencies above the gap. Below the gap, it is necessary to compute a number of elementary integrals. The result is

$$\begin{aligned}\epsilon_1(q,\omega)&=\epsilon_1^L(q,\omega_-),\quad |\omega|\geq\lambda\omega_F\\ &=1+\frac{2}{q_F a_0\pi}\left[\frac{1}{Q^2}-\frac{\Delta}{2Q^3}\left[\tan^{-1}\frac{2Q+Q^2}{\Delta}+\tan^{-1}\frac{2Q-Q^2}{\Delta}\right]\right.\\ &\qquad\left.+\left[\frac{\Delta^2}{8Q^5}+\frac{1}{2Q^3}-\frac{1}{8Q}\right]\ln\left[\frac{\Delta^2+(2Q+Q^2)^2}{\Delta^2+(2Q-Q^2)^2}\right]\right],\quad |\omega|<\lambda\omega_F\end{aligned} \tag{3.3}$$

where $Q=q/q_F$, and the positive quantity Δ is defined as $\Delta^2=\lambda^2-\omega^2/\omega_F^2$. (Here q_F and ω_F are the Fermi wave vector and frequency of a noninteracting electron gas of the same density.) The Kramers-Krönig relation guarantees that $\epsilon_1\geq 1$ for frequencies below the gap. Hence, there can be no plasmons in this frequency regime. In analogy with Eq. (3.2), we derive the sum rule

$$\int_0^\infty \operatorname{Im}\frac{1}{\epsilon(q,\omega)}\omega\, d\omega=-\tfrac{1}{2}\pi\omega_p^2\ . \tag{3.4}$$

Also, from Eq. (3.3), the long-wavelength limit of the dielectric function is simply

$$\epsilon(0,\omega)=1+\frac{\omega_p^2}{(\lambda\omega_F)^2-\omega^2}\ . \tag{3.5}$$

In Fig. 1, we compare our model dielectric function to the results of Walter and Cohen's calculation of the dielectric function of silicon in the static limit[13] and to the results of the Penn model.[18] We describe silicon in our model by the choice of parameters $r_s=2.0$ and $\lambda=0.4$. We choose r_s from the average density of the valence electrons in silicon; λ is obtained by matching to the static long-wavelength dielectric constant using Eq. (3.5). We feel that the agreement is quite good considering the simplicity of our model. Specifically, the

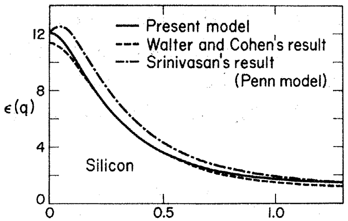

FIG. 1. Static dielectric functions $\epsilon(q,\omega=0)$ for Si from three calculations.

static limit of our dielectric function agrees more closely with the realistic Walter and Cohen calculation[13] than the Penn model.[18] Further, the model dielectric function is in semiquantitative agreement with the frequency and wave-vector-dependent dielectric function of Walter and Cohen.[14]

IV. EXCHANGE-CORRELATION POTENTIAL

In this section, we follow the formulation given in Sec. II using the model dielectric function to determine a one-parameter family of local-density exchange-correlation potentials. The heart of the Singwi *et al.*[5] calculation involves improving upon the self-consistent-field description of the electron gas by excluding the self-field of an electron in the determination of the dielectric response in an approximate way. In the present work, we make the ansatz that the model dielectric function describes not the electron gas but rather some isotropic semiconductor in the self-consistent-field approximation. The ansatz has some foundation because, as seen in the preceding section, the model function reduces to the Lindhard function (a self-consistent-field approximation) in the limit of vanishing λ and because of the reasonable agreement with the detailed self-consistent-field calculation of Walter and Cohen.[13,14] In particular, we require that the irreducible polarizability be given by

$$\begin{aligned}\pi^0(q,\omega) &= -\frac{q^2}{4\pi e^2}Q_0(q,\omega)\\ &= -\frac{q^2}{4\pi e^2}[\epsilon_{\text{model}}(q,\omega)-1]\ .\end{aligned} \tag{4.1}$$

We use the expression for Q_0 in lieu of its electron-gas counterpart in Eq. (2.3). Our calculation proceeds identically to that of Singwi and coworkers. We relate the exchange-correlation energy to the exchange-correlation potential with the expression[7]

$$V_{\text{xc}}(r_s,\lambda)=E_{\text{xc}}(r_s,\lambda)-\frac{r_s}{3}\frac{dE_{\text{xc}}(r_s,\lambda)}{dr_s}\ , \tag{4.2}$$

which is simply Eq. (2.7) for homogeneous systems. Moreover, for convenience in comparing our result with previous work, we present the results in terms of the parameter given by [22]

$$V_{\text{xc}}(r_s,\lambda)=-\frac{3}{\pi}\left[\frac{9\pi}{4}\right]^{1/3}\frac{\alpha(r_s,\lambda)}{r_s}\ . \tag{4.3}$$

The calculated $\alpha(r_s,\lambda)$ for selected values of r_s and λ are presented in Fig. 2.

From a scaling argument due to Slater,[23] we may generate the exchange part of the potential using Eq. (4.3) with $\alpha(r_s,\lambda)$ replaced by $\alpha(0,\lambda)$. Hence, from Fig. 2, we may study the values of the exchange potential for the system by considering $\alpha(0,\lambda)$ and the effect of correlation on the potential by considering the deviations of $\alpha(r_s,\lambda)$ from the exchange values. We find that the exchange potential deepens with increasing λ whereas the correlation potential weakens with increasing λ.

We begin by considering the correlations. By scaling, an increase in r_s is similar to an increase in the strength of the electron-electron coupling constant e^2. Imagine a system changing adiabatically under the influence of an increasing coupling constant. The final ground state will admix with some of the formerly unoccupied states. Therefore, the noninteracting system will provide an increasingly better description of the interacting system if there are increasingly fewer low-lying quantum states. In the present theory, this is the case of finite λ. Next, we turn to the exchange potentials. In a real semiconductor, the presence of the energy gaps is related to the external potential arising from the ion core. There is some occupancy of plane waves with wave vectors larger than the Fermi wave vector of the electron-gas system. Since the size of the exchange hole is determined by the shortest wavelengths among the occupied states, one would expect exchange holes in semiconductors to be somewhat smaller than their metallic counterparts. In Figs. 3 and 4, typical results for the present model are shown. We present the pair-correlation function in the combination

$$f(r;r_s,\lambda)=(q_Fr)^2[1-g(r;r_s,\lambda)] \tag{4.4}$$

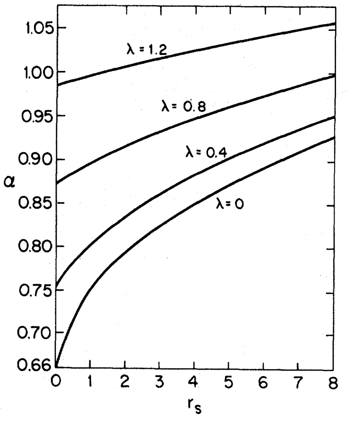

FIG. 2. Calculated exchange-correlation coefficient (see text) as a function of r_s and for selected λ.

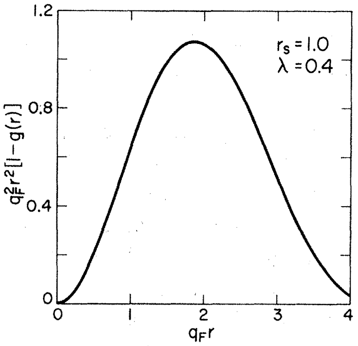

FIG. 3. Pair correlation function for a model semiconductor with $r_s = 1.0$ and $\lambda = 0.4$ in the combination $(q_F r)^2[1-g(r)]$.

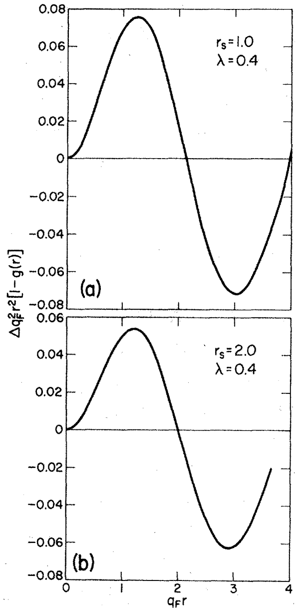

FIG. 4. Calculated difference curves of $q_F^2 r^2[1-g(r)]$ between an electron liquid and a model semiconductor with $\lambda = 0.4$ at (a) $r_s = 1.0$ and (b) $r_s = 2.0$.

for $r_s = 1$ and $\lambda = 0.4$ in Fig. 3 and the difference functions $f(r;r_s,\lambda) - f(r;r_s,0)$ for $\lambda = 0.4$ and $r_s = 1.0$ and $r_s = 2.0$ in Fig. 4. The difference function compares the present theory for the case of finite λ to the electron gas. The positive sign of the difference function at small r reflects the decrease in the exchange-correlation hole radius at finite λ. The double-lobe structure occurs because the exchange-correlation hole always contains one electron.[24] With the charge of the exchange-correlation hole conserved, the smaller hole radius results in a deeper exchange potential at larger λ.

A previous work by Aymerich and Mula[25] used the same approach as in this section but chose a plasmon-pole dielectric function. In contrast to our results, they find the exchange potential to be independent of the gap parameter. However, because the plasmon-pole approximation is sensitively dependent upon the choice of the plasmon dispersion coefficient, we feel that this approach is not useful for model calculations of the exchange-correlation potential.

For convenience, we have summarized our results in an interpolation formula for $\alpha(r_s,\lambda)$. The data in Table I are polynomial coefficients in the expression

$$\alpha(r_s,\lambda) = \sum_{i=0}^{3} \sum_{j=0}^{4} a_{ij} \lambda^i r_s^j \, . \tag{4.5}$$

These coefficients have no analytical significance and merely represent the results of the present calculation over the range $r_s = 0-15$ and $\lambda = 0-1.4$. The fit is accurate to better than 0.001 on the average and better than 0.01 in the worst case.

V. APPLICATION TO SILICON

We have performed a calculation on the band structure of silicon using the exchange-correlation potential of the present theory with $\lambda = 0.4$ as well

TABLE I. Polynomial coefficients for the interpolation Eq. (4.5). The polynomial is only valid for the exchange-correlation potential in the range $r_s \le 15$ and $\lambda \le 1.4$.

	r_s^0	r_s^1	r_s^2	r_s^3	r_s^4
λ^0	0.674 70	0.070 735	−0.008 9999	0.000 650 38	−0.000 017 748
λ^1	0.155 81	−0.068 905	0.013 3638	−0.001 120 43	0.000 033 193
λ^2	0.159 46	0.015 315	−0.006 3970	0.000 609 69	−0.000 018 358
λ^3	−0.062 46	0.001 706	0.000 8765	−0.000 092 46	0.000 002 492

TABLE II. Silicon energy eigenvalues in eV. (The $\Gamma_{25'}$ state is set at 0 eV.)

	LAPW[a]	$\lambda=0$	$\lambda=0.4$	Experiment[b]
Γ_1	-12.02	-11.94	-11.88	-12.5 ± 0.7
$\Gamma_{25'}$	0.00	0.00	0.00	0
$\Gamma_{15,c}$	2.49	2.58	2.67	$3.3-3.4$
$\Gamma_{12,c'}$	3.18	3.08	3.12	4.20
X_1	-7.84	-7.81	-7.78	
X_4	-2.82	-2.84	-2.79	-2.5 ± 0.3
$X_{1,c}$	0.55	0.75	0.90	
$L_{2'}$	-9.64	-9.57	-9.53	-9.3 ± 0.4
L_1	-7.06	-6.92	-6.85	-6.8 ± 0.2
$L_{3,c'}$	-1.16	-1.20	-1.18	-1.2 ± 0.2
$L_{3,c}$	1.40	1.55	1.64	
$L_{1,c}$	3.37	3.45	3.55	3.8,3.9
indirect gap		0.56	0.70	$1.11-1.17$

[a] Reference 29.

[b] Reference 30.

as for an electron-gas potential ($\lambda=0$). The calculation used a norm-conserving pseudopotential[26] in the pseudopotential band-structure program described in earlier work.[27] The pseudopotential "quality parameter" r_c was taken to be 0.75.[26] Plane waves up to 11 Ry in energy were considered which represent 169 plane waves at the zone center and similar numbers throughout the zone. The band structure was determined self-consistently to 0.01 eV using ten "special points"[28] in the irreducible $\frac{1}{48}$th of the Brillouin zone.

Our results, along with a recent linearized augmented plane-wave (LAPW) calculation of silicon by Hamann[29] and experiment results,[30] are presented in Table II. The agreement between the pseudopotential calculation with an electron-gas local functional and the LAPW calculation is good. We obtain differences of no more than 0.25 eV for states up to 5 eV above the top of the conduction band ($\Gamma_{25'}$). The exchange-correlation potential of the present theory produces a marginally (but consistently) better band structure than using the exchange-correlation potential derived from the electron gas, However, the measured gaps are excited-state properties of the systems, and our potential is only for the ground state. Also, with $\lambda=0.4$, Si is a nearly-free-electron system. Whether or not the present theory could help resolve some of the differences between experiment and theory in wide gap materials such as solid xenon or sodium chloride remains an open question.

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