Dielectric screening theory in the local-density-functional formalism. Application to silicon using Slater exchange

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(Received 8 December 1980)

The expression for the dielectric matrix, in the local-density-functional formalism, is evaluated for silicon using self-consistent pseudopotential electron energies and wave functions with the Slater exchange-correlation functional. The influence of the local-field effects as well as of the exchange-correlation correction is discussed. The long-wavelength limit of the exchange-correlation correction is determined and compared with existing calculations.

On the basis of the Hohenberg-Kohn[1] theorem, one can derive[2] an expression for the dielectric matrix in the local-density-functional formalism:

$$\epsilon = 1 - V_c \widetilde{X}(1 - V_x \widetilde{X})^{-1} . \tag{1}$$

The matrices V_c and V_x are defined by

$$V_c(\vec{q},\vec{G},\vec{G}') = \delta_{\vec{G}\vec{G}'} \frac{1}{\Omega} \int d\vec{r} \frac{1}{|\vec{r}-\vec{r}'|} e^{-i(\vec{q}+\vec{G})\cdot\vec{r}} , \tag{2}$$

and

$$V_x(\vec{q},\vec{G},\vec{G}') = \frac{1}{\Omega} \int d\vec{r} \int d\vec{r}' e^{-i(\vec{q}+\vec{G})\cdot\vec{r}}$$
$$\times \frac{\delta V_{xc}}{\delta\rho} e^{-i(\vec{q}+\vec{G}')\cdot\vec{r}'} , \tag{3}$$

with

$$V_{xc} = \frac{\delta(\rho E_{xc}[\rho])}{\delta\rho} , \tag{4}$$

where $E_{xc}[\rho]$ is the exchange-correlation energy of a uniform electron gas of density $\rho(\vec{r})$. The polarizability matrix $\widetilde{X}$ is given by the well-known expression[3]

$$X(\vec{q},\vec{G},\vec{G}') = \frac{1}{\Omega} \sum_{1,2}' \frac{\eta_1 - \eta_2}{E_1 - E_2} \langle 1 | e^{-i(\vec{q}+\vec{G})\cdot\vec{r}} | 2 \rangle$$
$$\times \langle 2 | e^{i(\vec{q}+\vec{G}')\cdot\vec{r}} | 1 \rangle . \tag{5}$$

Although the density in most solids is not slowly varying everywhere, the local density formalism was quite successful in describing various electronic properties.[4] However, not much attention has been paid to linear-response theory consistent with the one-electron equations used to describe the electronic states. For semiconductors a number of calculations exist[5] which use the random-phase approxima-

tion (RPA) (time-dependent Hartree)[3] form of the dielectric function (or matrix) together with local density or Hartree-Fock wave functions. Also a few calculations on metals have been performed.[6] It is obvious that Eq. (1) is reduced to the RPA case[7] if no exchange is taken into account, i.e., V_x is put equal to zero. Equation (1) is similar to an expression for the dielectric function of the uniform electron gas first given by Hubbard[8] to describe approximately exchange and correlation effects:

$$\epsilon(\vec{q},\omega) = 1 - \frac{V_c(\vec{q})\widetilde{X}(\vec{q})}{1 - G(\vec{q},\omega)V_c(\vec{q})\widetilde{X}(\vec{q})} . \tag{6}$$

There are, however, two major differences. First, because in the present treatment the perturbation is static, there is no frequency dependence in our $G(\vec{q},\omega)$. Second, Eq. (1) is more general in the sense that it includes lattice effects which result from the fact that all quantities V_c, V_x, $\widetilde{X}$, and ϵ are matrices.

The theory given above is applied to silicon. For the exchange-correlation potential V_{xc} we take the form given by Slater[9]

$$V_{xc}(\vec{r}) = -\frac{3}{2} \left[\frac{3}{\pi} \right]^{1/3} \rho^{1/3}(\vec{r}) . \tag{7}$$

Although in principle this approximation only takes exchange effects into account, it is generally accepted to be a good approximation for the exchange-correlation potential.[4] Using this functional the matrix $V_x(\vec{q},\vec{G},\vec{G}')$ [Eq. (3)] is simplified to

$$V_x(\vec{q},\vec{G},\vec{G}') = - \left[\frac{3}{\pi} \right]^{1/3} \frac{1}{\Omega} \int dr \rho^{-2/3}(\vec{r})$$
$$\times e^{-i(\vec{G}-\vec{G}')\cdot\vec{r}} , \tag{8}$$

i.e., the matrix elements are independent of $\vec{q}$ and

are a function of the difference of the reciprocal-lattice vectors $\vec{G}$ and $\vec{G}'$.

The Kohn-Sham equation is solved self-consistently using the pseudopotential scheme. First an ionic potential of the Topp-Hopfield type is chosen. The determination of its parameters is described in Ref. 10. The total crystal pseudopotential is then expanded in a Fourier series, retaining only a small number of Fourier components. The rest of the computational procedure can be summarized as follows:

(1) Start with an empirical pseudopotential (e.g., Cohen-Bergstresser).

(2) Diagonalize H and calculate ρ.

(3) Compute $V_{ion} + V_H + V_{xc}$.

(4) Go back to step 2 and compare the new charge density with the old one. Repeat this step until convergence is reached.

In the present case the convergence is rapid, i.e., after eight cycles the maximal relative difference of the charge density is less than 10^{-4}. In this calculation, 65 plane waves are treated exactly while an additional 150 are used in the Löwdin-Brust scheme.[11] The wave functions and energies are subsequently used in Eqs. (5) and (8) to construct $\tilde{X}$ and V_x. The calculation is performed for different values of the wave vector $\vec{q}$ in the [100] direction. Results of $\epsilon(\vec{q},0,0)$ are shown in Fig. 1 both for the RPA (Hartree) and the Slater case. It is seen from Fig. 1 that the effect of exchange correlation is an upward shift of the dielectric function ranging from 0% (at $\vec{q} = 0$) to 28% (around the Brillouin-zone boundary). The difference between the RPA and Slater dielectric functions is displayed in Fig. 2. The value
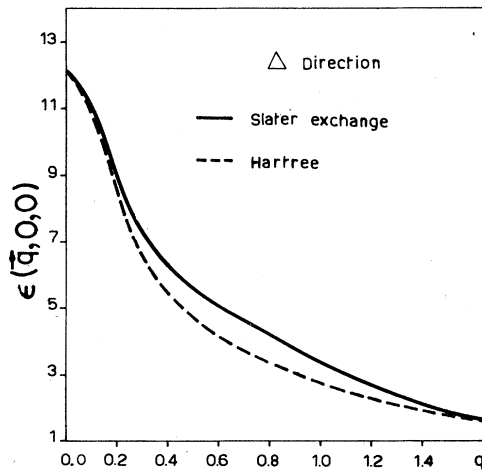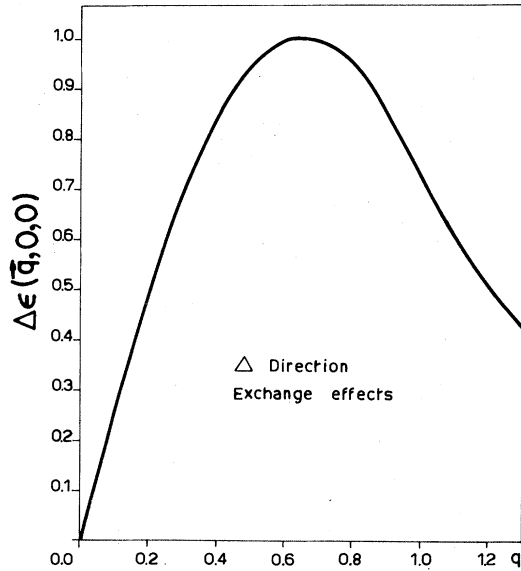

FIG. 2. Exchange effects in the microscopic dielectric function of silicon in the Δ direction. Horizontal axis in units of $2\pi/a$.

of $\epsilon(\vec{q},0,0)$ at $\vec{q} = 0$ is 12.1047 and should not be compared with the experimental value of 12.0.[12] This is owing to the local-field effects which are responsible for the matrix nature of the quantities in Eq. (1). The macroscopic dielectric function ϵ_m is given by[7]

$$\epsilon_m(\vec{q}) = \frac{1}{\epsilon^{-1}(\vec{q},0,0)} . \qquad (9)$$

FIG. 1. Microscopic dielectric function of silicon in the Δ direction. Full line: Slater exchange; broken line : RPA. Horizontal axis in units of $2\pi/a$.
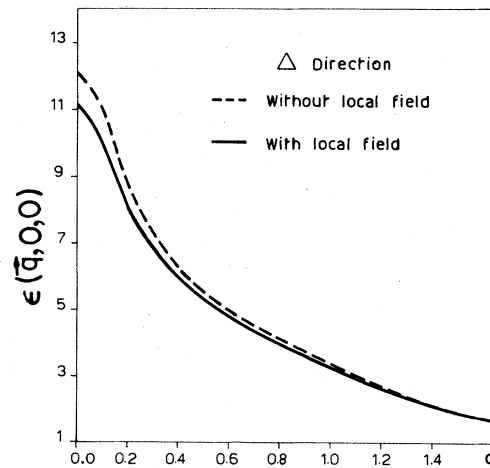

FIG. 3 Dielectric function of silicon in the Δ direction using Slater exchange. Full line: with local-field effects; broken line: without local-field effects. Horizontal axis in units of $2\pi/a$.

It is this quantity which should be compared with the experimental values.

The dielectric matrix is calculated for the first three stars, i.e., its dimension is 27. The macroscopic dielectric function is determined using Eq. (9) and is shown in Fig. 3 together with the microscopic dielectric function. The value of the macroscopic dielectric constant, including exchange effects, is found to be 11.0702. The value of the RPA macroscopic dielectric constant is 11.2788. So the local-field effects are 6.82% and 8.55%, respectively, in the RPA and the Slater approximation. In the theory of the free-electron gas it is customary to define[13] a quantity γ via the relation

$$\lim_{\vec{q}\to 0} G(\vec{q},0) = \frac{q^2}{k_F^2} \ . \tag{10}$$

The corresponding relation in the Slater linear-response theory is

$$\lim_{\vec{q}\to 0} \frac{V_x(\vec{q},0,0)}{V_c(\vec{q},0,0)} = \gamma \frac{q^2}{k_F^2} \ . \tag{11}$$

For silicon a value of $\gamma = 0.4603$ is found. Although the charge density in silicon is highly nonuniform, it is interesting to note that the corresponding value of γ for a uniform electron gas (with density $r_s = 2$) in the Hartree-Fock approximation[14] is 0.25, while in the Hubbard approximation[8] one finds 0.5.

In summary, in this paper the microscopic dielectric matrix and the macroscopic dielectric function of silicon is calculated using the Slater functional together with a self-consistent pseudopotential band calculation. The influence of local-field effects and of exchange-correlation effects is discussed. The long-wavelength limit of the exchange-correlation correction is also calculated.

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