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Model dielectric matrices for quasiparticle self-energy calculations

Mark S. Hybertsen
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

Steven G. Louie
Department of Physics, University of California, Berkeley, California 94720

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A computationally simple model for the full static dielectric matrices is proposed for use in self-energy calculations to obtain quasiparticle energies and band gaps. The screening hole around an added electron at a given point in the crystal is approximated by the screening response of a homogeneous medium determined by the local density. The resulting approximation to the screening potential includes the crucial part of the local fields. When used with the previously developed self-energy approach, quasiparticle energies and band gaps in good agreement with experimental results are obtained for diamond, Si, and Ge.

It has recently been possible to calculate the quasiparticle energies and band gaps in semiconductors and insulators accurately from first principles.[1,2] The approach is based on evaluating the electron self-energy operator (Σ) in the *GW* approximation.[3] Then the quasiparticle energies are obtained directly. The crucial features of this approach have been identified[1] to include adequate treatment of the full crystalline Green's function, the local fields in the screening, and the dynamical screening response of the electrons. The electron self-energy operator is intrinsically a nonlocal operator, an aspect which is essential to obtain properly the gap energy in semiconductors and insulators.[1,2] Despite the success of this approach, it is computationally quite demanding. Recent applications to surface states[4] and optical properties of semiconductor superlattices[5] represent the most complex systems accessible to this approach to date.

The commonly used local-density-functional approach[6,7] (LDA) for band-structure calculations has the advantage of computational tractability and is therefore widely used. However, the resulting band energies are not formally justified as quasiparticle energies. Indeed, the most glaring discrepancy is the underestimate of the minimum gap in semiconductors and insulators by 30–100%, the "band-gap problem."[8] It is desirable to have a well-founded approach for quasiparticle energies which is also comparable to the LDA in computational difficulty. The original proposal of Sham and Kohn[9] for a density functional for Σ has recently been implemented for semiconductors by Wang and Pickett.[10] There have been several other recent proposals,[11-13] some of which[11,12] attempt to reduce Σ in semiconductors to a form related to the local density through $\rho^{1/3}$. Unfortunately, none of these proposals has been demonstrated to be quantitatively reliable for a wide range of materials *and* in comparison to all the experimental data for a given material, e.g., photoemission, inverse photoemission, and optical data. Godby, Schluter, and Sham[14] have fitted their self-energy results to a simple nonlocal form for Σ, but have not yet found a constructive model.

In the present paper, we propose an important simplification of the self-energy approach. Rather than model Σ directly, the full crystalline Green's function and the nonlocality of Σ are retained. We propose a model for the screened Coulomb interaction. This is a computationally demanding step in the full calculation.[1] The resulting approach is not as simple as previous proposals, but as seen below, it is well founded theoretically and demonstrably works for the test cases of diamond, Si, and Ge. The present results for band gaps and band dispersions agree with the full self-energy calculations within about 0.1–0.2 eV. The computational effort is significantly reduced in this approach, although treatment of the self-energy operator and quasiparticle energies given the present model dielectric matrices is still more difficult than LDA calculations.

Our approach is based on a simple observation. In the self-energy calculation, the most important aspect of the local fields is the variation of the depth of the screening response to an the added electron with its location. The depth of the static screening potential in this case generally follows the magnitude of the local charge density.[15] We therefore, propose that the screening potential around an added electron at $\mathbf{r}'$ can be approximated for these purposes by that which would be induced in an electron gas of the local density at $\mathbf{r}'$. That is, the range of the screening hole around an added electron at $\mathbf{r}'$ is approximately determined from the local density at that point.[16] The total amount of charge expelled from the region around the added electron is determined by ϵ_0. Thus, the depth of the screening potential near $\mathbf{r}'$ will smoothly follow the magnitude of the density $\rho(\mathbf{r}')$. Regions of high density, e.g., the bonds in semiconductors, will screen the added electron more effectively than regions of low density, e.g., outside the bond chain. $V_{\mathrm{scr}}(\mathbf{r},\mathbf{r}')$ should in general be symmetric under interchange of $\mathbf{r}$ and $\mathbf{r}'$. In the present model, this is maintained by an explicit symmetrization as described below. Consequently, the model screening hole is in general anisotropic as it should be with weight shifted towards the regions of higher electron density. This model is obviously exact in the limit of a uniform electron gas.

The viability of these ideas is demonstrated in Figs. 1

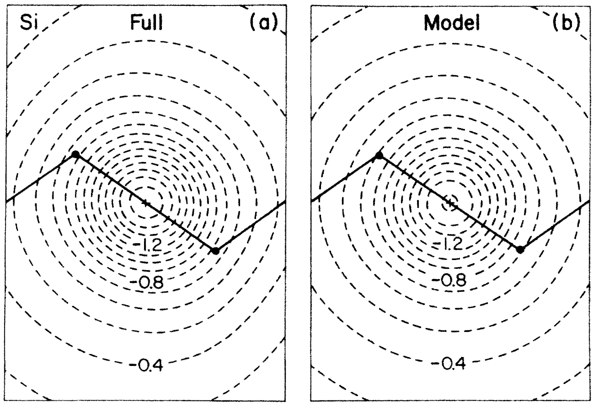

FIG. 1. The static screening potential around an added electron at the bond center in Si is shown as calculated from (a) the full *ab initio* dielectric matrices and (b) the present model. The contour plots (in intervals of 0.1 Ry) are displayed in the $(1\bar{1}0)$ plane with the bond chain indicated schematically.

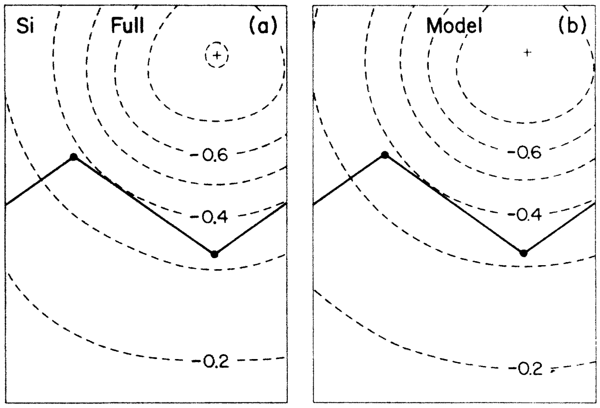

FIG. 2. The same as in Fig. 1 for an added electron in the interstitial region.

and 2, for the case of Si. Here, the screening potential around an added electron is shown for two cases: the added electron at the bond center (Fig. 1); and the added electron in the interstitial region (Fig. 2). Part (a) of each figure shows the screening potential computed using *ab initio* static dielectric matrices as previously reported.[15] Part (b) shows the results based on the present model. It can be seen that the present model reproduces the local fields quantitatively.

In general,[17] the quasiparticle energies are determined by solution of

$$[T+V_{\mathrm{ext}}(\mathbf{r})+V_H(\mathbf{r})]\Psi(\mathbf{r})+\int d\mathbf{r}'\Sigma(\mathbf{r},\mathbf{r}';E^{qp})\Psi(\mathbf{r}')=E^{qp}\Psi(\mathbf{r}), \quad (1)$$

where the terms correspond to the kinetic energy, the external potential due to the ion cores, the average electrostatic (Hartree) potential, and the electron self-energy operator, respectively. We use the *GW* approximation[3] for Σ:

$$\Sigma(\mathbf{r},\mathbf{r}';E)=\frac{i}{2\pi}\int d\omega e^{-i\delta\omega}G(\mathbf{r},\mathbf{r}';E-\omega)W(\mathbf{r},\mathbf{r}';\omega), \quad (2)$$

where δ is a positive infinitesimal. The full crystalline Green's function G and dynamically screened Coulomb interaction W enter. For the Green's function, a quasiparticle approximation is used as has been detailed previously.[1] The screened Coulomb interaction is given by

$$W(\mathbf{r},\mathbf{r}';\omega)=\frac{1}{\Omega}\int d\mathbf{r}''\epsilon^{-1}(\mathbf{r},\mathbf{r}'';\omega)V_c(\mathbf{r}''-\mathbf{r}'), \quad (3)$$

where ϵ^{-1} is the time-ordered dielectric matrix and V_C is the bare Coulomb interaction. In our first-principles approach,[1] the dielectric matrices were obtained in two steps: (i) the *ab initio* static dielectric matrices were calculated using the local-density-functional approach;[15] (ii) the dielectric matrices were extended to finite frequency using a generalized plasmon-pole model employing exact sum rules.[1]

In the present paper, we approximate the static dielectric matrices and then proceed exactly as before. Our model for the screening response in the crystal is

$$V_{\mathrm{scr}}(\mathbf{r},\mathbf{r}')=\tfrac{1}{2}[V_{\mathrm{scr}}^{\mathrm{hom}}(\mathbf{r}-\mathbf{r}';r_s(\mathbf{r}'))+V_{\mathrm{scr}}^{\mathrm{hom}}(\mathbf{r}'-\mathbf{r};r_s(\mathbf{r}))], \quad (4)$$

where r_s is the usual density parameter evaluated at the position of the added electron. The average taken in Eq. (4) enforces the proper symmetry under interchange of $\mathbf{r}$ and $\mathbf{r}'$. The local screening response is determined by an approximate dielectric function. We use the Levine-Louie model dielectric function appropriate for a semiconductor:[18]

$$\epsilon_{LL}(q)=1+\frac{2}{\pi q_F}\left[\frac{1}{Q^2}-\frac{\lambda}{2Q^3}\left(\tan^{-1}\frac{2Q+Q^2}{\lambda}+\tan^{-1}\frac{2Q-Q^2}{\lambda}\right)+\left(\frac{\lambda^2}{8Q^5}+\frac{1}{2Q^3}-\frac{1}{8Q}\right)\ln\left(\frac{\lambda^2+(2Q+Q^2)^2}{\lambda^2+(2Q-Q^2)^2}\right)\right]. \quad (5)$$

Here $Q=q/q_F(r_s)$ and the parameter $\lambda(r_s)$ is determined from

$$\lambda^2(r_s)=\omega_p^2(r_s)/\omega_F^2(r_s)(\epsilon_0-1). \quad (6)$$

For each $\mathbf{r}'$, the parameters (plasma frequency and Fermi energy) are evaluated at the local density r_s. The model requires as input the value of the dielectric constant of the material. It can in principle be calculated, but in practice is taken from experiment. The Levine-Louie model is used with the dielectric constant fixed throughout. The parameter λ which formally enters should not be interpreted as a local gap in the present context. It is a parameter which insures the correct long-range screening in the system. Physically, only $1-1/\epsilon_0$ electrons are expelled from the region of the added electron in a semiconductor. This incomplete screening must be properly included in the self-energy operator, particularly the screened exchange term.

It is straightforward to manipulate Eq. (4) to obtain the dielectric matrices for the crystal. Using a reciprocal lattice vector-basis, one obtains

$$\epsilon_{GG'}^{-1}(\mathbf{q};\omega=0)V_c(\mathbf{q}+\mathbf{G}')=\frac{1}{2}\left[V_c(\mathbf{q}+\mathbf{G})\int d\mathbf{r}'\epsilon_{LL}^{-1}[|\mathbf{q}+\mathbf{G}|;r_s(\mathbf{r}')]e^{i(G'-G)\cdot\mathbf{r}'}\right.$$
$$\left.+V_c(\mathbf{q}+\mathbf{G}')\int d\mathbf{r}\epsilon_{LL}^{-1}[|\mathbf{q}+\mathbf{G}'|;r_s(\mathbf{r})]e^{i(G'-G)\cdot\mathbf{r}}\right]. \quad (7)$$

In this model, the diagonal portion of the dielectric matrix is an average over the local screening response at different points in the crystal. Equation (7) is straightforward to implement in practice. Each row of the dielectric matrix for a given **q** can be obtained by using a fast-Fourier transform. The second term is just the Hermitian conjugate of the first. No use need be made of crystal symmetry as the calculation is quite fast for an arbitrary **q**. (Crystal symmetry could be exploited both in setting up the real space values for the fast Fourier transforms and to eliminate some of the rows which need be calculated.)

This new approximation for the static screening response has been used to calculate quasiparticle energies for diamond, Si, and Ge. In each case, a dielectric constant must be chosen as input. We have used the experimental values of $\epsilon_0=5.5$, 12, and 16, respectively.[19] The final results are rather insensitive to the exact choice made. In particular, the gap energies change by less than 0.1 eV when ϵ_0 is varied from 11 to 14 for the case of Si.

The resulting quasiparticle energies and band gaps are compared to our previous first-principles calculations[1] and experiment[20] in Tables I-III. The overall agreement is quite good, generally within 0.1-0.2 eV of the full theory and experiment. The calculated gaps are a little too small using the model while the valence-band width is broader. (The direct gap in diamond is exceptional in that regard, being somewhat larger.) One should note that the LDA gaps calculated for these materials are 3.9, 0.5, and $\lesssim 0$ eV for diamond, Si and Ge, respectively. We stress that a full range of available experimental data is included in the comparison made in Tables I-III.

The approach of Wang and Picket,[10] which contains two parameters, gives the correct band gap for diamond and moderately accurate results for Si (e.g., a direct gap at Γ of $E_g^{\mathrm{dir}}=3.07$ eV and an indirect gap of $E_g=0.93$ eV) but has not been successfully applied to the more demanding case of Ge. Neither of the $\rho^{1/3}$ theories[11,12] have been explicitly evaluated for a wide range of materials and band energies for comparison to experiment. The two-plane-wave-based model[13] which also has several parameters does not yield the indirect gaps but does give $E_g^{\mathrm{dir}}=7.7$ eV (3.3 eV) for diamond (Si).

TABLE I. Comparison of the calculated quasiparaticle energies and gaps for diamond using the present model (Model) to previous full calculations (Full) and experiment.

	Theory		
	Full[a]	Model	Expt.[b]
E_g	5.6	5.5	5.48
$\Gamma_{1v}\rightarrow\Gamma_{25'v}$	23.0	24.2	24.2 ± 1, 21 ± 1
$\Gamma_{25'v}\rightarrow\Gamma_{15c}$	7.5	7.6	7.3

[a] Reference 1. [b] Reference 20.

In the present model, the magnitude of the matrix element at the valence band maximum (VBM), $\langle \mathrm{VBM}|\Sigma|\mathrm{VBM}\rangle$, is reproduced within 0.4, 0.3, and 0.2 eV of the full calculation for diamond, Si, and Ge, respectively. This corresponds to only a 2-3% difference and as seen from Tables I-III, the quasiparticle energies relative to the valence-band edge are within 0.1-0.2 eV of the full theory. If the common division of the self-energy operator into screened exchange and Coulomb hole terms is made, $\Sigma=\Sigma_{SX}+\Sigma_{CH}$, we find that the excellent agreement results in part from cancellation of somewhat larger errors for the individual terms. For instance, in the case of Si, these terms are −3.56 and −8.41 eV in the full calculation of Ref. 1 while using the present model we find −4.00 and −7.73 eV respectively. The Σ_{SX} term is too large in magnitude, indicating that the exchange operator is underscreened. The Σ_{CH} term is too small, also consistent with less effective screening. These errors cancel to some degree so that the model is only off by 0.3 eV for the total. Similar cancellation occurs for the gaps which involve differences between self energies: the SX contribution is overestimated while the CH contribution is underestimated.

We expect that the present model will be of great help in calculations for more complex systems. In particular, surfaces and superlattices are very demanding systems with considerable experimental interest. For these heterogeneous systems, the model requires a dielectric constant at each point. We suggest that the appropriate way to use our model in these cases is with an ϵ_0 appropriate to the material in the immediate neighborhood of a particular point. For example, in a superlattice *AB*, the dielectric constant of material *A* would apply in the *A* region and

TABLE II. Same as Table I for Si.

	Theory		
	Full[a]	Model	Expt.[b]
E_g	1.29	1.16	1.17
$\Gamma_{1v}\rightarrow\Gamma_{25'v}$	12.04	12.45	12.5 ± 0.6
$\Gamma_{25'v}\rightarrow\Gamma_{15c}$	3.35	3.32	3.4
$\Gamma_{25'v}\rightarrow\Gamma_{2'c}$	4.08	4.14	4.2
$X_{4v}\rightarrow\Gamma_{25'v}$	2.99	3.09	2.9, 3.3 ± 0.2
$L_{3'v}\rightarrow\Gamma_{25'v}$	1.27	1.31	1.2 ± 0.2, 1.5
$\Gamma_{25'v}\rightarrow L_{1c}$	2.27	2.22	2.1, 2.4 ± 0.15
$\Gamma_{25'v}\rightarrow L_{3c}$	4.24	4.19	4.15 ± 0.1
$L_{3'v}\rightarrow L_{1c}$	3.54	3.53	3.45
$L_{3'v}\rightarrow L_{3c}$	5.51	5.50	5.50

[a] Reference 1. [b] Reference 20.

TABLE III. Same as Table I for Ge.

	Theory		
	Full[a]	Model	Expt.[b]
E_g	0.75	0.60	0.744
$\Gamma_{6v}\rightarrow\Gamma_{8v}$	12.86	13.06	12.6, 12.9 ± 0.2
$\Gamma_{8v}\rightarrow\Gamma_{7c}$	0.71	0.62	0.89
$\Gamma_{8v}\rightarrow\Gamma_{6c}$	3.04	2.91	3.006
$\Gamma_{8v}\rightarrow\Gamma_{8c}$	3.26	3.13	3.206
$X_{5v}\rightarrow\Gamma_{8v}$	3.22	3.28	3.15 ± 0.2, 3.5 ± 0.2
$\Gamma_{8v}\rightarrow X_{5c}$	1.23	1.06	1.3 ± 0.2
$L_{6v}\rightarrow\Gamma_{8v}$	1.61	1.64	1.4 ± 0.3
$L_{4,5v}\rightarrow\Gamma_{8v}$	1.43	1.46	
$\Gamma_{8v}\rightarrow L_{6c}$	4.33	4.19	4.3 ± 0.2, 4.2 ± 0.1
$\Gamma_{8v}\rightarrow L_{4,5c}$	4.43	4.29	
$\Gamma_{8v}\rightarrow L_{6c}$	7.61	7.43	7.8 ± 0.6, 7.8 ± 0.1

[a] Reference 1. [b] Reference 20.

that of material *B* in the *B* region with some smooth interpolation near the interfaces within about a bond length. For the self-energy operator, it is the local screening hole that is crucial. Therefore, the charge expelled from the immediate region of the added electron must be correct. Longer-range effects due to material heterogeneity are of limited importance for Σ but alter ϵ_0 for the heterogeneous system.

In summary, we have developed a model for the screening response of semiconductors which works quite well in conjunction with the self-energy approach for quasiparticle energies and band gaps. This allows a considerable computational saving for calculation of the quasiparticle energies while maintaining the quantitative results. The present model should allow treatment of complex systems more readily and should also extend to the case of metals.

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[20] Reference 19 provides a general set of data. A more detailed discussion of the data in Tables I–III is provided in Ref. 1 along with references to recent experiments.