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Presented at the 17th International Conference
on the Physics of Semiconductors,
San Francisco, CA, August 6-10, 1984;
and to be published in the Proceedings

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July 1984

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Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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This work was supported by a program development fund from the Director of the Lawrence Berkeley Laboratory under Contract Number DE-AC03-76SF00098 and by NSF Grant Number DMR8319024.

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The electronic excitation energies have been calculated for Si using the *ab initio* pseudopotential approach and the screened exchange-coulomb hole approximation for the electron self energy. Within the approximation of neglecting local field effects in screening the coulomb interaction, the direct gaps are found to be in much better agreement with experiment than standard density functional calculations. We argue that the inclusion of local field effects are necessary to reproduce the band dispersions and hence the indirect gap.

Theoretical determination of the optical gaps in semiconductors from first principles remains a difficult problem. The most commonly used treatment of exchange and correlation is the density functional approach.[1] The eigenvalues from the resulting effective one-body equations are often interpreted, without justification, as excitation energies. Results for simple metallic systems are reasonable but the gaps in semiconductors and insulators are underestimated by 30-50%.[2] Several approaches to this problem are currently being investigated by various groups, mostly by looking at the electron self energy operator (Σ) directly. Wang and Pickett have used a density functional approach with a local approximation for Σ in Si with good results for the direct gaps, although the band dispersions and hence indirect gap are less well reproduced.[3] Hanke and coworkers have done extensive work on a formulation which includes short range local field effects as well as diagrams beyond RPA in the dynamical screening of the coulomb interaction in Σ. They have applied this to diamond with good results.[4] It is conceptually and computationally simplest to remain close to a one-particle picture. Phillips proposed a generalization of Koopman's theorem where the most important contribution to the quasiparticle energy corresponds to replacing the exchange operator in Hartree-Fock by a dynamically screened exchange operator, within the approximation that relaxation effects are negligible.[5] Neglecting local field effects and using a static approximation, this is equivalent to considering Σ evaluated in the screened exchange-coulomb hole (SX-CH) approximation,[6] since the CH contribution is constant. Early calculations for Si were done using this approach by Brinkman and Goodman[7] and by Kane.[8]

Our approach to calculation of the excitation energies in Si follows that of Phillips and Kleinman[9] and Kane.[10] We report here the results of precise calculations done for the prototypical semiconductor Si using an *ab initio* pseudopotential approach and the SX-CH approximation. Neglecting local field effects in screening the coulomb interaction, we still find that the direct gaps are improved but that the band dispersions are not in agreement with experiment. We discuss the importance of local field effects, particularly for the CH contribution, based on first principles calculation of the full dielectric matrix. This is the first step in a systematic study of excitation energies in semiconductors.

Excitation energies are obtained by solving the quasiparticle equation:[6]

$$(T + V_{ext} + V_H)\psi_{n\vec{k}}(\vec{r}) + \int d^3r'\, \Sigma(\vec{r}, \vec{r}'; E_{n\vec{k}})\psi_{n\vec{k}}(\vec{r}') = E_{n\vec{k}}\psi_{n\vec{k}}(\vec{r}) \qquad (1)$$

where V_{ext} is the external potential, V_H is the Hartree potential, and Σ is the Dyson mass operator. In our approach we use selfconsistent solutions of the effective one body equations in the density functional approach[1] as a basis set for expanding the quasiparticle wavefunction. Then Eq. (1) for a given $\vec{k}$ reduces to solution of the secular equation

$$\det\left[(\epsilon_{n\vec{k}} - E)\delta_{n,n'} + <n\vec{k}|\Sigma(\vec{r},\vec{r}';E) - V_{xc}^{DF}(\vec{r})|n'\vec{k}>\right] = 0 \tag{2}$$

where $\epsilon_{n\vec{k}}$ is the corresponding eigenvalue of the density functional equation and V_{xc}^{DF} is the exchange-correlation potential in density functional theory which we evaluate in a local density approximation.[1] The wavefunctions and eigenvalues $\epsilon_{n\vec{k}}$ are obtained using the *ab initio* pseudopotential method with a plane wave expansion for the wavefunctions.[11,12]

The GW approximation[6] is used to evaluate Σ

$$\Sigma(\vec{r}_1,\vec{r}_2;\omega) = i\int \frac{d\omega'}{2\pi}\, G(\vec{r}_1,\vec{r}_2;\omega-\omega')\int d^3r_3\, \frac{e^2}{|\vec{r}_1-\vec{r}_3|}\epsilon^{-1}(\vec{r}_3,\vec{r}_2;\omega') \tag{3}$$

where the coulomb interaction is screened by the inverse dielectric function ϵ^{-1} and G is the full one-particle Green's function. The Green's function is written in the form

$$G(\vec{r}_1,\vec{r}_2;\omega) = \sum_{n_1,\vec{k}_1} \frac{\psi_{n_1\vec{k}_1}(\vec{r}_1)\psi^*_{n_1\vec{k}_1}(\vec{r}_2)e^{i\delta\omega}}{\omega - \epsilon_{n_1\vec{k}_1} + i\delta\epsilon_{n_1\vec{k}_1}} \tag{4}$$

where $\delta \to 0^+$ and energies are measured from the fermi level. In practice, the density functional calculation gives excellent charge densities and optical excitation energies that are within $\sim$1 eV of experiment for Si so we assume that the corresponding wavefunctions are a good approximation to $\psi_{n\vec{k}}$. These are used to evaluate the Green's function. Since we are primarily interested in the region near the gap (small compared to the plasma energy) the frequency integration can be approximated to give the SX-CH approximation to Σ:[6,10]

$$\Sigma_{SX}(\vec{r}_1,\vec{r}_2) = -\sum_{n_1,\vec{k}_1}^{occ} \psi_{n_1\vec{k}_1}(\vec{r}_1)\psi^*_{n_1\vec{k}_1}(\vec{r}_2)\int d^3r_3 \frac{e^2}{|\vec{r}_1-\vec{r}_3|}\epsilon^{-1}(\vec{r}_3,\vec{r}_2;0) \tag{5a}$$

$$\Sigma_{CH}(\vec{r}_1,\vec{r}_2) = \delta^3(\vec{r}_1-\vec{r}_2)\int d^3r_3 \frac{e^2}{|\vec{r}_1-\vec{r}_3|}\,\frac{1}{2}\left[\epsilon^{-1}(\vec{r}_3,\vec{r}_2;0) - \delta^3(\vec{r}_3-\vec{r}_2)\right] \tag{5b}$$

The SX contribution has the structure of a static screened exchange operator and the CH contribution gives the interaction of the electron with its induced charge. We write the required matrix elements in Eq. (2) in reciprocal space:

$$<n\vec{k}|\Sigma_{SX}|n'\vec{k}> = -\sum_{n_1}^{occ}\sum_{\vec{q},\vec{G},\vec{G}'} <n\vec{k}|e^{-i(\vec{q}+\vec{G})\cdot\vec{r}}|n_1\vec{k}+\vec{q}> \frac{4\pi e^2\epsilon^{-1}_{\vec{G}\vec{G}'}(\vec{q})}{|\vec{q}+\vec{G}|^2} <n_1\vec{k}+\vec{q}|e^{i(\vec{q}+\vec{G}')\cdot\vec{r}}|n'\vec{k}> \tag{6a}$$

$$<n\vec{k}|\Sigma_{CH}|n'\vec{k}> = \sum_{\vec{q},\vec{G},\vec{G}'} \frac{2\pi e^2}{|\vec{q}+\vec{G}|^2}\left[\epsilon^{-1}_{\vec{G}\vec{G}'}(\vec{q}) - \delta_{\vec{G}\vec{G}'}\right] <n\vec{k}|e^{i(\vec{G}'-\vec{G})\cdot\vec{r}}|n'\vec{k}> \tag{6b}$$

where the sum on $\vec{q}$ is over the Brillouin zone and the $\vec{G}$ are reciprocal lattice vectors. The dielectric matrix is taken in the standard way.

As a first approximation, we neglect local field effects in the screening (off diagonal elements of the dielectric matrix) and use the Levine-Louie model dielectric function for the diagonal part.[13] It reproduces well the numerically calculated RPA dielectric function in Si. In this case, the CH contribution from Eq. (6b) reduces to a constant for $n = n'$ and zero otherwise. The off diagonal matrix elements of the remaining $\Sigma_{SX} - V_{xc}^{DF}$ in Eq. (2) are found to be negligible, affecting the quasiparticle energies by less than .06 eV. This justifies *a posteriori* our replacement of the quasiparticle wavefunction by the one-particle wavefunction from the density functional calculation in the evaluation of the Green's function. The sum over the Brillouin zone is done with a special points scheme where $q = 0$ is included in the set. The singularity in Eq. (6a) for $q = 0$ is handled approximately as in Ref. 6. The resulting quasiparticle energies are displayed for states near the gap in Table I. These results are converged to better than .1 eV with respect to the sum

Table I. Comparison of the calculated band energies (in eV relative to the valence band maximum) within the density functional theory and the present approach to experiment for Si.

	LDA	Present Work	EXP.[a]
$\Gamma_{25',v}$	0.00	0.00	0.0
$\Gamma_{15,c}$	2.57	2.98	3.40
$\Gamma_{2',c}$	3.29	4.14	4.2
$X_{4,v}$	-2.86	-3.33	-2.9
$X_{1,c}$	0.71	0.58	1.30[b]
$L_{3',v}$	-1.21	-1.39	-1.2±.2
$L_{1,c}$	1.55	1.88	2.1[c]
$L_{3,c}$	3.40	3.74	3.9
$X_{4,v} \rightarrow X_{1,c}$	3.57	3.91	4.25[d]
$L_{3',v} \rightarrow L_{1,c}$	2.76	3.27	3.4[d]
$L_{3',v} \rightarrow L_{3,c}$	4.61	5.13	5.5

[a] Ref. 14 except where noted.
[b] Estimated from the conduction band minimum and longitudinal effective mass.
[c] Ref. 15. [d] Ref. 16.

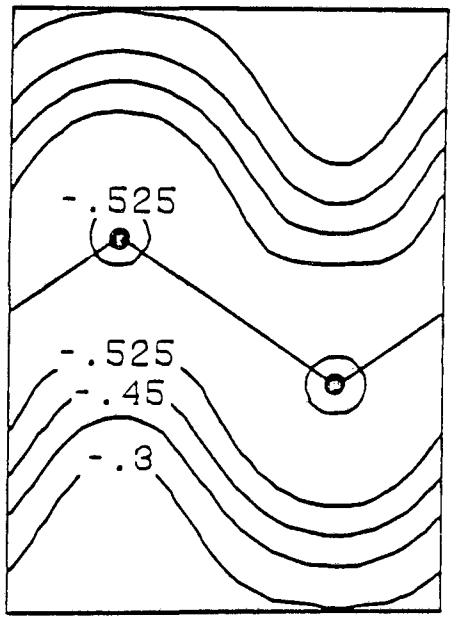

Figure 1. Contour plot of the effective local potential that enters the CH term upon inclusion of local field effects in the (1$\bar{1}$0) plane for Si. The bond chain is shown for clarity and the contour interval is 0.075 Ry.

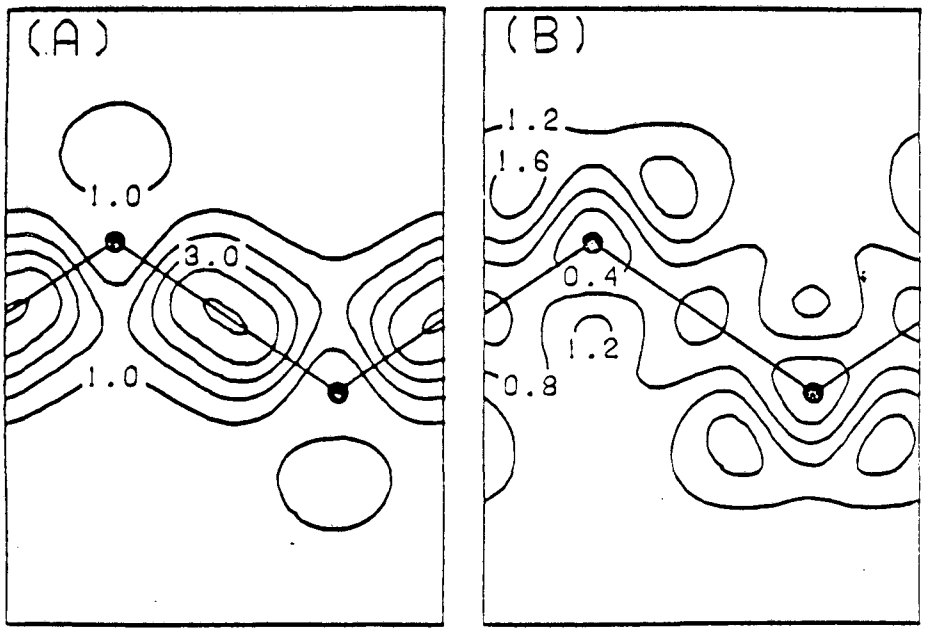

Figure 2. Contour plot of the square of the wavefunction in the (1$\bar{1}$0) plane of Si for (a) the $\Gamma_{25',v}$ complex and (b) for the $X_{1,c}$ complex. Contour interval is 1.0 electrons per cell for (a) and 0.4 electrons per cell for (b).

displayed for states near the gap in Table I. These results are converged to better than .1 eV with respect to the sum over the Brillouin zone and the number of planewaves in the wavefunctions. The direct gaps agree much better with experiment than the corresponding density functional eigenvalues displayed for reference. The band dispersions and indirect gap are, however, in worse agreement.

We believe, for physical reasons, that it is important to include local field effects in the screening. The interaction of an electron with its induced charge represented by the CH depends on the location of the electron in the unit cell. From Eq. (6b), the CH is the interaction of the charge in state $n\bar{k}$ with a local effective potential. We have plotted that effective potential in the $(1\bar{1}0)$ plane of Si in Fig. 1. The full dielectric matrix required to generate Fig. 1 was calculated within the RPA based on the *ab initio* pseudopotential calculation used above. The resulting dielectric matrix gives a calculated dielectric constant of ~ 14 compared to ~ 12 from experiment. In generating Fig. 1, the required sum over the Brillouin zone was approximated with three points in the irreducible part of the zone and the dielectric matrix was cut off at $\sim 59 \times 59$. Fig. 2 shows contour plots of the square of the wavefunction for the $\Gamma_{25'v}$ complex (a) and the X_{1c} complex (b). The spatial variation in the effective potential in the CH contribution will lead directly to different matrix elements for the valence band maximum and conduction band minimum: the $\Gamma_{25'v}$ states are peaked in the bond region (density ~ 5 electrons per cell at the bond center) where as the X_{1c} states are spread out through the cell (density ~ 1 electron per cell in the interstitial region). In general, preliminary results indicate that the CH term cancels part of the effect of the SX term for the valence band states and enhances the effect for conduction band states. Thus gaps will generally be opened up but valence band dispersions should change less as compared to the density functional results.

Note added in proof: Results of calculations based on the full dielectric matrix as above give both valence and conduction band energies in good agreement with experiment.

Acknowledgements- We thank Dr. J. C. Phillips for bringing his work on screened exchange to our attention. This work is supported by NSF Grant No. DMR8319024 and by a program development fund from the Director of the Lawrence Berkeley Laboratory. MSH acknowledges the support of an IBM fellowship.

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This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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