Metal-Insulator Transition in Kohn-Sham Theory and Quasiparticle Theory

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We investigate the pressure-induced metal-insulator transition of silicon in the diamond structure. Quasiparticle theory (QPT) calculations are performed within the *GW* approximation, and Kohn-Sham theory (KST) results are obtained by using an exchange-correlation potential derived from the *GW* self-energy operator, not using the common local-density approximation (LDA). In both KST and the LDA metallization occurs at a much larger volume than in QPT. These results suggest that the metallization point and Fermi surface of the Kohn-Sham electrons are *not* necessarily those of the real system.

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Density-functional theory[1] (DFT), though widely used in so-called "electronic structure" calculations, is in fact a theory of the electronic ground state: It is formulated to reproduce the ground-state electron density and total energy. However, all practical implementations[2] of DFT use the Kohn-Sham theory[3] (KST) in which a Schrödinger equation for an effective system of noninteracting electrons is solved. It is interesting to ask to what extent the resulting one-electron energies agree with the excited-state energies of the system calculated within quasiparticle theory (QPT).

Something is known about this already. First, the highest occupied KST eigenvalue is known to equal the true ionization potential of the system.[4,5] For infinite systems, this is the chemical potential μ. Second, the minimum band gap is not equal to the KST minimum gap (the gap in the KST one-electron band structure). In the bulk semiconductors Si, GaAs, AlAs, and diamond[6] their difference (the discontinuity Δ in the exchange-correlation potential on addition of one electron[7-9]) is a significant fraction of the band gap.

Perhaps the most fundamental question about the excited electronic states of a solid is whether the solid is a metal or an insulator. It might be conjectured that the Kohn-Sham electrons in exact KST will become metallic at the same volume as the real solid, and even that they will have the same Fermi surface as the real system. A typical argument might run as follows. When a metallic system is subjected to a static perturbation the induced charge density exhibits Friedel oscillations whose form is characteristic of the quasiparticle Fermi surface. As exact DFT must give the correct density response to a static perturbation, it might be thought that the Kohn-Sham Fermi surface is the same as the quasiparticle Fermi surface. However, these arguments are invariably based on the linear response theory of the Kohn-Sham electrons and the real system, and can be seen to break down in the following way. The density response function of the system, χ, to a static additional external potential, δV_{ext}, is certainly a quantity that can be calculated using DFT, since the induced electron density, δn, must be reproduced. However, it is *not* the same as the density response function of the fictitious system of noninteracting electrons (the Kohn-Sham electrons). The former is given by[10] $\delta n = \chi \delta V_{\text{ext}}$, while the latter is given by $\delta n = \chi_{\text{KST}} \delta V_{\text{eff}}$, where V_{eff} is the Kohn-Sham effective potential, which includes the Hartree and exchange-correlation potentials. Using DFT one can show that χ and χ_{KST} are related by[11]

$$\chi = (1 - \chi_{\text{KST}} v - \chi_{\text{KST}} K_{\text{xc}})^{-1} \chi_{\text{KST}}, \tag{1}$$

where v is the Coulomb interaction $1/(\mathbf{r}-\mathbf{r}')$ and K_{xc} is the "exchange-correlation kernel" $\delta V_{\text{xc}}(\mathbf{r}')/\delta n(\mathbf{r})$. It is the presence of this last term, K_{xc}, which causes the argument to break down. Since it is known that V_{xc} is a highly nonanalytic functional of the electron density (for example, V_{xc} has a discontinuity upon addition of an electron to a semiconductor[6]) the relationship between χ and χ_{KST} may not be simple. In particular, it cannot be assumed that χ will be metallic [$\chi(\mathbf{q},\mathbf{q},\omega=0)$ tending to a constant as the wave vector $q \to 0$] merely because χ_{KST} is metallic. In fact, the possibility of nonanalyticities in the denominator means that χ may be insulator-like (tending to zero like q^2 as $q \to 0$) at the same time that χ_{KST} is metallic.

The possibility is supported by recent work on two models of interacting electron systems. Schönhammer and Gunnarsson[12] have shown that, in a weakly correlated two-dimensional Hubbard model, the KST and QPT Fermi surfaces are different. Also, a metal-insulator transition in a model "cubic electron gas" was shown to be absent from the corresponding Hartree-Fock and exchange-only DFT's.[13] Of course, the KST and QPT transitions *may* coincide in particular systems. For example, a study[14] of a model one-dimensional semiconductor using a two-plane-wave basis set showed that within these approximations the metallization transition was at the same point in KST and QPT. Also, the KST and QPT Fermi surfaces of jellium can be shown to be identical.[12,15]

To various degrees, the four models mentioned above are all artificial. It remains to be seen whether the Fermi surfaces of *real* materials are given correctly by KST. Of the four models, jellium is the closest to a real material, and so it might be expected that little or no difference would exist between KST and QPT Fermi surfaces of nearly-free-electron-like materials. If this is so, KST can still be used to calculate reasonably accurate Fermi surfaces for a variety of real systems.

In this work we investigate whether KST can distinguish between a metal and an insulator in a realistic system. We do this by reducing the volume of silicon in the diamond structure until it becomes a metal. We have performed calculations for three different unit-cell volumes: $V/V_0=1.00$, 0.90, and 0.78, where V_0 is the equilibrium volume at zero pressure. KST calculations using the local-density approximation (LDA) for exchange and correlation[16] at a large number of volumes indicate that the LDA band gap becomes zero at $V/V_0=0.78$. The top of the valence band is at Γ at each of the volumes studied. The bottom of the conduction band is on the line Γ-X at $0.84X$ at the equilibrium volume $V/V_0=1.00$, and it moves only slightly to $0.88X$ when the volume is reduced to $V/V_0=0.78$.

Our approach is to perform a calculation of the electronic structure of the systems using computational many-body theory, and then calculate a KST exchange-correlation potential. We first calculate the self-energy $\Sigma(\mathbf{r},\mathbf{r}',\omega)$ in the GW approximation[17]

$$\Sigma(\mathbf{r},\mathbf{r}',\omega)=\frac{i}{4\pi}\int_{-\infty}^{\infty}e^{i\omega\delta}W(\mathbf{r},\mathbf{r}',\omega')\times G(\mathbf{r},\mathbf{r}',\omega+\omega')d\omega' , \quad (2)$$

where the Green's function G is approximated by its LDA counterpart, the screened Coulomb interaction W is obtained within the random-phase approximation from LDA calculations,[6] and δ is an infinitesimal. We then calculate the quasiparticle energies (the energy required to add an electron or hole to the system) by solving the quasiparticle equation

$$[-\tfrac{1}{2}\nabla^2+V_{\text{ext}}(\mathbf{r})+V_H(\mathbf{r})-E_i]\psi_i(\mathbf{r})+\int\Sigma(\mathbf{r},\mathbf{r}',E_i)\psi_i(\mathbf{r}')d^3r'=0 . \quad (3)$$

To solve this equation we use first-order perturbation theory in $\Sigma(E)-V_{\text{xc}}^{\text{LDA}}$, starting from the LDA wave functions and energies, which we know to be well converged because of the consistently small size of the second-order term in test calculations, indicating the closeness of the quasiparticle and LDA wave functions. We also use Σ to calculate the KST exchange-correlation potential $V_{\text{xc}}(\mathbf{r})$ using the exact relationship[7,9]

$$\text{Im}\int_{-\infty}^{\mu}[G_{\text{KST}}(\omega)\cdot\{\Sigma(\omega)-V_{\text{xc}}\}\cdot G(\omega)]_{\mathbf{r}=\mathbf{r}'}d\omega=0 , \quad (4)$$

in which G and G_{KST} are approximated by the LDA Green's function and $[\,]_{\mathbf{r}=\mathbf{r}'}$ denotes matrix multiplication inside the brackets with the $\mathbf{r}=\mathbf{r}'$ matrix element then taken. The KST eigenvalues which would be obtained if this V_{xc} were used instead of the LDA are then calculated using first-order perturbation theory, this time in $V_{\text{xc}}-V_{\text{xc}}^{\text{LDA}}$. [The discrepancy between the LDA and QPT gaps is of little importance in calculating V_{xc}: Even in the extreme case of $V/V_0=0.78$ we find that artificially increasing the LDA band gap from zero to its QPT value by adding a constant to all the conduction-band energies in G in Eq. (4) alters the KST band gap by less than 0.1 eV.] The basic technique of the calculations is similar to that of Ref. 6, although several technical improvements have been made.[18] The LDA calculations used about 250 plane waves and sixty special $\mathbf{k}$ points to obtain a converged potential, while the calculations of the self-energy operators and exchange-correlation potentials were done using 169 plane waves and six special points.

We chose to study silicon because it is convenient for our pseudopotential techniques and is known to be a material for which the GW approximation yields an accurate band structure. Real silicon undergoes a structural phase transition to the β-tin structure at a volume of approximately[19] $V/V_0=0.91$, and so the transition that we are studying would not be seen. However, our system is one of real atoms interacting in a realistic manner, and the transition we study is typical of "electronic" metallization transitions. The fact that the existence of a lower-energy structure prevents the metal-insulator transition that we have studied from being observed experimentally is of little importance for our purposes, and has no effect on the reliability of our approximations. Other materials, less suitable for our methods, may undergo metallization transitions within a single structure. For example, fcc xenon has been studied experimentally and theoretically.[20]

Our calculations are not exact solutions of the many-body problem, and we must ask to what extent the approximations made influence the results. Various approximations have been mentioned earlier in this Letter, but we have concluded that their effects on the results are small. However, we have not discussed the validity of the central approximation: the GW approximation for the self-energy. It is known that the GW approximation gives an excellent description of the excitation energies of many semiconductors with a wide range of equilibrium volumes, including silicon, and also of covalent and metallic solids.[6,21] It is therefore reasonable to suppose that the GW description of silicon at a volume of $V/V_0=0.78$ is as good as that at $V/V_0=1.00$, since both more and less metallic materials are described well. Thus we conclude that our calculated self-energies describe the electronic properties of a system very like silicon. (Although the effects of excitons and of the formation of electron-hole droplets[22] on the transition are not included in the GW approximation, these are important on the scale of 0.1 eV considered here.) Furthermore, one can view the use of the GW approximation as just a way of calculating a realistic self-energy. The KST

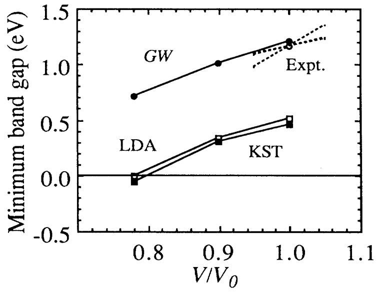

FIG. 1. The calculated minimum band gap of silicon in the diamond structure, plotted against the unit-cell volume. The gaps were calculated using (i) the LDA, (ii) quasiparticle theory (*GW*), and (iii) "accurate" Kohn-Sham theory (KST). The points are joined to guide the eye. The open circle and dashed lines show the experimental minimum band gap and the experimental values of its volume dependence (Ref. 23) at equilibrium.

exchange-correlation potential is obtained directly from the self-energy via Eq. (4), and thus our conclusion that the KST and QPT Fermi surfaces are different is independent of our use of the *GW* approximation. We have tried to use a self-energy containing a realistic description of the electron-electron interaction in a solid so that the *size* of the effects that we calculate is relevant for real materials.

The dependence of the minimum band gap in each of the three types of calculation of the unit-cell is summarized in Fig. 1. As was already known,[6] at the equilibrium volume the quasiparticle band gap (which agrees with the measured band gap to within about 0.1 eV) is about 100% larger than the LDA band gap, while the KST band gap is very close to the LDA gap (reflecting the remarkable similarity between these two potentials). As the volume is reduced, the LDA, KST, and QPT minimum gaps all decrease, but at approximately the same rate. At smaller volumes, the curves remain almost parallel. We therefore conclude that the volume at which the band gap of the noninteracting electrons in KST becomes zero is quite different from the volume at which the actual (QPT) metallization transition occurs, though it is quite close to the "metallization" volume given by the LDA. The respective volumes are given in Table I. Figure 2 shows the direct gap at X, where again the KST gap error remains roughly constant as the volume is reduced.

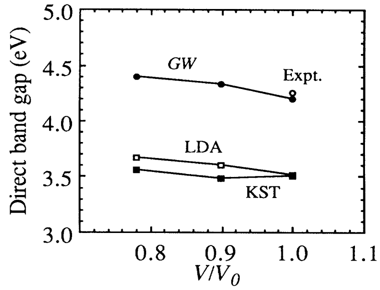

FIG. 2. The calculated direct band gaps of silicon in the diamond structure at X, plotted against the unit-cell volume. The gaps were calculated using (i) the LDA, (ii) quasiparticle theory (*GW*), and (iii) "accurate" Kohn-Sham theory (KST). The points are joined to guide the eye. The open circle shows the experimental direct band gap.

It has been observed before[24] that LDA pressure dependences of band gaps are substantially more accurate than the band gaps themselves. This is confirmed by our results. The volume derivatives of the band gaps, which have been calculated from a quadratic fit and converted to pressure derivatives by use of the experimental bulk modulus[23] (0.988 Mbar), are given in Table II. The pressure derivatives are in agreement with experiment. (Because small differences are involved, the numerical uncertainty in the LDA and *GW* derivatives is about ±0.3 ev/Mbar. More accurate results, in the LDA only, are available elsewhere.[25] The KST pressure derivatives are not given, since the numerical uncertainty in these differences is large.)

In summary, we have shown that the metallization volume of silicon in the diamond structure is substantially different in Kohn-Sham theory from its true quasiparticle value. Δ, the discontinuity in the exchange-correlation potential on addition of an electron, which is equal to the inherent KST gap error, remains nonzero even when the Kohn-Sham gap is zero. This result is not compatible with the conjecture that the metallization

TABLE I. The "metallization volume", V_m, of silicon (defined as the volume at which the band gap vanishes) expressed as a fraction of the equilibrium volume, V_0, in (i) the LDA, (ii) quasiparticle theory (*GW*) and (iii) "accurate" Kohn-Sham theory.

Calculation	V_m/V_0
LDA	0.78
Quasiparticle theory	0.5[a]
Kohn-Sham theory	0.80

[a] Approximation: extrapolated from the data of Fig. 1.

TABLE II. The pressure derivatives of the band gaps of silicon at equilibrium in (i) the LDA, (ii) quasiparticle theory (*GW*), and (iii) experiment.

	dE_g/dp (eV/Mbar)		
Band gap	LDA	*GW*	Expt.[a]
Minimum gap	−1.3	−1.8	−1.6, −1.41 ± 0.06, −3.8
Γ	0.5	0.6	···
X	−0.9	−1.6	···

[a] Reference 23.

transition volume in KST is the same as that of the real system, thereby implying that the real Fermi surface is not necessarily identical in all respects to that of the Kohn-Sham electrons.

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[1] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[2] See, for example, *Theory of the Inhomogeneous Electron Gas,* edited by S. Lundqvist and N. H. March (Plenum, New York, 1983), and references therein.

[3] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[4] M. Levy, J. P. Perdew, and V. Sahni, Phys. Rev. A **30**, 2745 (1984).

[5] C.-O. Almbladh and U. von Barth, Phys. Rev. B **31**, 3231 (1985).

[6] R. W. Godby, M. Schlüter, and L. J. Sham, Phys. Rev. Lett. **56**, 2415 (1986); Phys. Rev. B **36**, 3497 (1987); Phys. Rev. B **37**, 10159 (1988).

[7] L. J. Sham and M. Schlüter, Phys. Rev. Lett. **51**, 1888 (1983).

[8] J. P. Perdew and M. Levy, Phys. Rev. Lett. **51**, 1884 (1983).

[9] L. J. Sham and M. Schlüter, Phys. Rev. B **32**, 3883 (1985).

[10] Here, and in other equations, matrix multiplication of nonlocal quantities is implied.

[11] We use hartree atomic uits ($h/2\pi = e = m_e = 4\pi\epsilon_0 = 1$) throughout.

[12] K. Schönhammer and O. Gunnarsson, Phys. Rev. B **37**, 3128 (1988).

[13] R. S. Jones and S. B. Trickey, Phys. Rev. B **36**, 3095 (1987).

[14] M. Lannoo, M. Schlüter, and L. J. Sham, Phys. Rev. B **32**, 3890 (1985).

[15] J. M. Luttinger, Phys. Rev. **119**, 1153 (1960).

[16] D. M. Ceperley and B. I. Alder, Phys. Rev. Lett. **45**, 566 (1980); parametrized in J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[17] L. Hedin and S. Lundqvist, in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1969), Vol. 23, p. 1.

[18] The most significant improvement combines much of the accuracy of the model-free imaginary-axis frequency integration of Ref. 6 with the efficiency of the plasmon-pole-model function used in *Physics of Group IV Elements and III-V Compounds,* edited by O. Madelung, M. Schulz, and H. Weiss, Landolt-Börnstein: Numerical Data and Functional Relationships in Science and Technology, New Series Group III, Vol. 17a (Springer, New York, 1982). This and other technical aspects will be described in a later paper.

[19] Jing Zhu Hu, Larry D. Merkle, Carmen S. Menoni, and Ian L. Spain, Phys. Rev. B **34**, 4679 (1986).

[20] M. Ross and A. K. McMahan, Phys. Rev. B **21**, 1658 (1980); A. K. Ray, S. B. Trickey, R. S. Weidman, and A. B. Kunz, Phys. Rev. Lett. **45**, 933 (1980).

[21] M. S. Hybertsen and S. G. Louie, Phys. Rev. Lett. **55**, 1418 (1985); Phys. Rev. B **32**, 7005 (1985); Phys. Rev. B **34**, 5390 (1986); W. von der Linden and P. Horsch, Phys. Rev. B **37**, 8351 (1988); J. E. Northrup, M. S. Hybertsen, and S. G. Louie, Phys. Rev. Lett. **59**, 819 (1987).

[22] W. F. Brinkman and T. M. Rice, Phys. Rev. B **7**, 1508 (1973).

[23] Madelung, Schultz, and Weiss, Ref. 18.

[24] S. B. Trickey, A. K. Ray, and J. P. Worth, Phys. Status Solidi (b) **106**, 613 (1981).

[25] M. Cardona and N. E. Christensen, Phys. Rev. B **35**, 6182 (1987).