First-order metal-insulator transition in band overlap mechanism

Takao Kotani
School of Materials, Arizona State University, Tempe, AZ, 85284

Rei Sakuma
Graduate School of Advanced Integration Science,
Chiba University, Chiba 263-8522, Japan
(Dated: September 23, 2008)

Abstract

We present a method to analyze the metal-insulator transition (MIT) due to the band overlap mechanism. It is based on a model with the knowledge of the homogeneous electron gas, combined with results based on the quasiparticle self-consistent $GW$ method. Because of the long-range nature of the Coulomb interaction, the MIT occurs as the first-order phase transition, that is, the band gap becomes negative (band overlap) suddenly at some critical lattice constant.

PACS numbers:
FIG. 1: (color online) Illustration of the first-order metal-insulator transition by the band overlap mechanism. The band gap $E_g$ is gradually being reduced when the lattice constant $a$ is getting smaller. Then it suddenly jumps to the metallic phase; the band overlap $E_{ovl}$ appears as shown by the broken line. In our method explained in Fig. 2 around (see text), we assume the rigid band shifts.

The metal-insulator transitions (MIT) is important not only for fundamental physics, but also for the high-pressure physics, or for its potential applicability to electrical or optical switches, e.g., YH3 [1]. Among the possible mechanisms of the MIT [2], we focus on the band-overlap mechanism which is the simplest in the sense that it is described within the one-particle picture. Here we present a theoretical treatment at zero temperature without phonons. The MIT is illustrated in Fig. 1 (we explain it below). Though the density functional theory (DFT) can give an one-particle picture represented by its Kohn-Sham eigenvalues and eigenfunctions, the eigenvalues cannot be identified as the quasiparticle energies (QPEs); it is well known that the DFT predicts too small $E_g$. The problem is not in the local density approximation (LDA) usually used in DFT; as shown by the calculations with the optimized effective potential method with the exact exchange plus correlation in the random phase approximation (EXX+RPA), Kotani showed that the true Kohn-Sham eigenvalues without LDA are only slightly larger than the eigenvalues in LDA for semiconductors [3]. It is confirmed by other groups recently [4].
Thus it is necessary to use a method beyond DFT to obtain the reasonable quasiparticle (QP) picture, or rather the one-particle static Hamiltonian $H^0$ which represent the QP. For example, for MIT for bcc Hydrogen, $GW$ calculations is used by Kioupakis, Zhang, Cohen, and Louie. The $GW$ approximation (GWA) is theoretically reasonable to obtain QPEs, however, the reliability of the usual GWA is limited because it is the one-shot (perturbative) calculations starting from the solution in LDA. This can cause a problem in cases; for example, we may get insulator solution in GWA starting from the metallic solution in LDA. In such a case, its reliability is questionable. This situation can be corrected by the self-consistent perturbation idea. In fact, they used a simplified version of the self-consistency to determine $U$ in the LDA+$U$+GW calculation as was done by Aryasetiawan and Gunnarsson. It is also used recently for the MIT problem for VO$_2$ by Sakuma Miyake and Aryasetiawan. However, such a self-consistency is only for a degree of freedom; a satisfactory version of self-consistency is formulated by the quasiparticle self-consistent $GW$ method (QSGW). Then all the degree of non-local static potential is determined self-consistently. We had shown that QSGW reproduce the band gap $E_g$ for wide range of semiconductors and insulators very well. Thus it is reasonable to apply QSGW to analyze the MIT for the band-overlap mechanism.

The QSGW is taken as an approximation to the rigorous theory. To see it, note that the self-consistent procedure in QSGW can be divided into two parts. One is the determination of the one-particle static Hamiltonian $H^0$ from the given Hartree potential plus self-energy $V_H + \Sigma(r, r', \omega)$, the other is the perturbative calculation of $V_H + \Sigma(r, r', \omega)$ in GWA starting from $H^0$. The former is a recipe to extract $H^0$ which represent the QP; note that iterative procedure is required to determine $H^0$ even for fixed $V_H + \Sigma(r, r', \omega)$ (see the norm minimization formalism). The latter can be replaced by the rigorous procedure at least as a thought experiment. If we were able to do it, we would have reached to the exact ground state with reasonable $H^0$. A practical method to improve QSGW is presented by Shishkin, Marsman and Kresse, where the excitonic effects (correlational motion of the electron-hole) are included in the polarization function when we evaluate the screened Coulomb interaction $W$. They succeeded to give systematic improvement for the overestimation of $E_g$ in the QSGW.

Here we present a method to analyze the MIT based on the knowledge of homogeneous electron gas in combination with the insulator solutions given by QSGW (or its extension).
As seen in Fig. 1, we have valence and conduction bands with $E_g$ for the insulator phase. $E_g$ is monotonically getting smaller when the lattice constant $a$ is being reduced by external pressure. If we have a first-order MIT, $E_g$ suddenly jumps from some positive value to the negative value (band overlap) at the critical lattice constant $a = a_c$. This occurs if the total energy for the metal phase becomes lower than that of the insulator. Then we see electron pocket in valence band and hole pocket in conduction band, which are specified by the Fermi energy $E_F$. Our analysis below shows that the first-order MIT is inevitably occur because of the nature of the long-range Coulomb interaction. Then we estimate the size of the transition for the case of fcc YH$_3$ based on the QSGW calculation for insulator phase.

Before looking into our model, let us remind the nature of the homogeneous electron gas [13, 14]. At lower density $n$ (density $n$ can be specified by $r_s$, $4\pi r_s^3/3 = 1/n$), the Coulomb interaction $v$ is more important than the kinetic energy. The exchange self-energy at $E^F$ as $\Sigma^x = -\frac{4}{3}0.916/r_s = -1.2218/r_s$ Ry dominates the kinetic energy $\epsilon^{\text{kin}} = |k^F|^2/(2m) = 3.6832/r_s^2$ Ry at low density (large $r_s$), where $k^F$ is the Fermi momentum. The Fermi energy is given as $E^F = \epsilon^{\text{kin}} + \Sigma^x + \Sigma^c$, where the Hartree term do not exist since it is cancelled by the background positive charge. These terms are evaluated at $E^F$ and at $k^F$ for given $n$. Because of the behavior of $\epsilon^{\text{kin}}$ and $\Sigma^x$, $E^F$ as function of $n$ is not monotonic. $\Sigma^x(n) \propto -n^{1/3}$ dominates $E^F$ for $n \to 0$, though $\epsilon^{\text{kin}} \propto n^{2/3}$ does $E^F$ for high $n$. $\Sigma^c$ enhances the effect of $\Sigma^x$ as seen in Table III in Ref. 13 by Hedin, where we see that $E^F$ is negative at $r_s \gtrsim 3$. This large negative values of $\Sigma^x + \Sigma^c$ overriding $\epsilon^{\text{kin}}$ at low $n$ means the energy gain due to the Fermi statistics and the correlational motion of electrons (or the structure of the full many-body eigenfunctions). Since the Coulomb interaction is stronger at $q \to 0$, the behavior of $E^F$ is quite anomalous at $n \to 0$. This is in contrast to models with short-range interaction, which is $q$-independent and we have $\Sigma^x \propto -n$. Then it can not dominate the kinetic term at low density.

We treat a simplified model to avoid difficulty in real systems. In principle, we treat both of the insulator and the metal phases within QSGW (or its extensions). However, in practice, simple sampling method for the Brillouin-zone summation [10] is not applicable to the metal phase because we need to use too many $k$ points to take into account the contributions from the small amount of holes in valence band (and electrons in conduction bands). To avoid this problem, we consider a model with simplified energy bands with some assumptions. At first, we have to prepare $H^0$ for the insulator phase by QSGW. When we
can observe the MIT, $H^0$ should show small $E_g$, which is decreasing as $a$ is being reduced.

In our model, we only take into account the bands around the Fermi energy as shown in Fig[1]. The valence bands are specified by the isotropic effective mass $m_{\text{val}}$ and its degeneracy $N_{\text{val}}$; the conduction band by $m_{\text{con}}$ and $N_{\text{con}}$. These parameters should be chosen so as to mimic the bands in the insulator phase given by QSGW. As we concentrate on the MIT, we only take into account the monotonic $a$-dependence in $E_g$; we assume $m_{\text{con}}$ and $m_{\text{val}}$ are not $a$-dependent. Further, we assume the rigid shift of energy bands (no deformations).

For the model, we consider the situation that some amount of electrons (specified by density $n$) are moved from the valence bands to the conduction bands. Then we treat two quasi-Fermi energies, $E_{\text{Fermi}}^{\text{val}}(n)$ for the electrons in valence bands, and $E_{\text{Fermi}}^{\text{con}}(n)$ for holes in conduction bands. As we discuss below, we will evaluate the total energy as function of $n$, and the energy minimum of the model occurs at some finite $n$ (thus metal) below some critical $E_g$.

$E_{\text{Fermi}}^{\text{val}}(n)$ and $E_{\text{Fermi}}^{\text{con}}(n)$ are defined as the changing rate of the total energy per adding (subtracting) an electron. Thus the total energy $\Delta E(n)$ relative to the insulator phase is given by an adiabatic connection as

$$\Delta E(n) = \int_0^n dn (E_g + E_{\text{Fermi}}^{\text{con}}(n) - E_{\text{Fermi}}^{\text{val}}(n)), \quad (1)$$

where we can set $E_{\text{Fermi}}^{\text{val}}(0) = E_{\text{Fermi}}^{\text{con}}(0) = 0$. Then $E_{\text{Fermi}}^{\text{con}}(n)$ is given as $E_{\text{Fermi}}^{\text{con}}(n) = \epsilon^{\text{kin}}(n) + \epsilon^{\text{Hartree}}(n) + \Sigma^x(n) + \Sigma^c(n)$. As we saw in the electron gas, $\epsilon^{\text{kin}}(n) = |k_F|^2/(2m_{\text{val}}) \propto n^{2/3}m_{\text{val}}$. The exchange part is given as $\Sigma^x = -1.2218/\bar{\varepsilon}r_s$, where $\bar{\varepsilon}$ means the effective dielectric constant representing the screening effect in the insulator phase, and $r_s$ is for the density $n$. We have to use $n/N_{\text{val}}$ instead of $n$ if $N_{\text{val}} \neq 1$. We treat $\bar{\varepsilon}$ as constant; $\bar{\varepsilon}$ is little dependent on $a$ in the case of indirect gap as in fcc YH3. For $\Sigma^c$, we use the RPA formula, e.g., see Eq.(86) in Ref.[13], where we use $W = v/\bar{\varepsilon}(q, \omega) = v/\bar{\varepsilon} \times 1/(1 - v\chi_0/\bar{\varepsilon})$. This $W$ is obtained in the RPA with $v/\bar{\varepsilon}$ instead of the bare Coulomb interaction $v$. $\chi_0$ here contains the contribution due to electrons in valence bands and due to holes in conduction bands, but no interband contributions; neglecting the interband contribution will be reasonable for the case with indirect gap. We neglect $\epsilon^{\text{Hartree}}$, because $\epsilon^{\text{Hartree}} \propto n$ can be neglected in comparison with $\Sigma^x$ at least for small $n$. We further neglect the other kind of correlational effect beyond QSGW as excitonic effects between electrons. With these assumptions, we can evaluate $E_{\text{Fermi}}^{\text{val}}(n)$ and also $E_{\text{Fermi}}^{\text{con}}(n)$ for given $m_{\text{val}}, N_{\text{val}}, m_{\text{con}}, N_{\text{con}}$, and $\bar{\varepsilon}$. In our model,
$\alpha$-dependence is only in $E_g$; the dependence cause just a constant shift in the integrand of Eq. (1) as function of $n$.

Let us look into the numerical results. In Fig. 2, solid line shows $E_{\text{F con}}(n) - E_{\text{F val}}(n)$ for the case $m_{\text{val}} = m_{\text{con}} = 1$ (in unit of electron mass), $N_{\text{val}} = N_{\text{con}} = 1$, and $\bar{\varepsilon} = 8$. Dotted line is without $\Sigma^c$ contribution. The difference of areas A–B shows the total energy difference between insulator and metal. When $E_g < 0.08$ eV, we have $B > A$ resulting the stability of the metal phase at Q. See text.

![Graph](image)

FIG. 2: Solid line shows $E_{\text{F con}}(n) - E_{\text{F val}}(n)$ for the case $m_{\text{val}} = m_{\text{con}} = 1$ (in unit of electron mass), $N_{\text{val}} = N_{\text{con}} = 1$, and $\bar{\varepsilon} = 8$. Dotted line is without $\Sigma^c$ contribution. The difference of areas A–B shows the total energy difference between insulator and metal. When $E_g < 0.08$ eV, we have $B > A$ resulting the stability of the metal phase at Q. See text.
TABLE I: Calculated size of MIT in our model. for given $\bar{\varepsilon}$, $m_{\text{val}}$, $m_{\text{con}}$, $N_{\text{con}}$, (we use $N_{\text{val}} = 1$). When $E_g$ is getting smaller and reach at $E_g = E_{cr}^g$, it cause the first-order phase transition to metal with the band overlap $E_{ovl}^{cr}$.

| $\bar{\varepsilon}$ | $m_{\text{val}}$ | $m_{\text{con}}$ | $N_{\text{con}}$ | $E_{cr}^g$ (eV) | $E_{ovl}^{cr}$ (eV) |
|----------------------|------------------|------------------|-----------------|----------------|-----------------|
| 8                    | 1                | 1                | 1               | 0.08           | -0.09           |
| 8                    | .5               | .5               | 1               | 0.04           | -0.05           |
| 8                    | 1                | 1                | 4               | 0.10           | -0.11           |
| 8                    | .5               | .5               | 4               | 0.05           | -0.05           |
| 4                    | .5               | .5               | 1               | 0.16           | -0.19           |
| 4                    | 1                | 1                | 1               | 0.32           | -0.38           |
| 4                    | .5               | .5               | 4               | 0.19           | -0.22           |
| 4                    | 1                | 1                | 4               | 0.39           | -0.44           |
| 8                    | .41              | .92              | 4               | 0.05           | -0.06           |
| 4                    | .41              | .92              | 4               | 0.21           | -0.24           |

rigid band shift (no band narrowing nor widening). The dotted line is without $\Sigma^c$; we see that the contribution from $\Sigma^c$ enhance $E_{cr}^g$ almost twice larger. Considering the behavior of $E_{\text{con}}^{\text{Fermi}}(n) - E_{\text{val}}^{\text{Fermi}}(n)$, this first-order phase transition can be a general phenomena for the band-overlap MIT.

In Table I calculated $E_{cr}^g$ and $E_{ovl}^{cr}$ are given for kinds $m_{\text{val}}, m_{\text{con}}, N_{\text{val}}$ and $\bar{\varepsilon}$. As $m_{\text{val}}$ and $m_{\text{con}}$ are heavier, $E_{cr}^g$ and $E_{ovl}^{cr}$ get larger because the contribution from kinetic term is smaller. $\bar{\varepsilon}$, which determines the size of the effective Coulomb interaction, can strongly affect on $E_{cr}^g$ and $E_{ovl}^{cr}$. We may overestimate $\Sigma^c$ a little in RPA, thus we does $E_{cr}^g$; this is indicated by the fact that $\Sigma^c$ for homogeneous electron gas given by the accurate method [15] is 69% of RPA value at $r_s=4$ (62% at $r_s=100$). The parameter set $m_{\text{val}} = .41, m_{\text{con}} = .92, N_{\text{con}} = 4$, and $\bar{\varepsilon} = 8$ is to mimic the energy bands of fcc YH3. Its bottom of conduction band is at $L$ point, where two Fermi surface exist, but we neglect the smaller one because it contains only $\sim10\%$ of electrons of bigger Fermi surface. The Fermi surface is anisotropic, but we take the simple average as $m_{\text{con}} = (m_x m_y m_z)^{1/3} = 0.92$. The valence top is at $\Gamma$, where it has one spherical Fermi surface. We will report how the band gap changes as the function of $a$ elsewhere together with other analysis for comparison with experiments [16]. In anyway, our result of $E_{cr}^g = 0.05\text{eV}$ should be taken as a semi-quantitative prediction.
since our model treatment is very simplified.

Though our MIT mechanism may occur in reality, we have not found experiments which are directly related to our MIT mechanism. As we discuss elsewhere[16], the MIT for YH3 observed in experiments will be mainly controlled by the structural transition, thus the band-overlap mechanism here will be not directly related to the experiments. In the case of GdN [17], the MIT explained here might occur. See Fig.2 in Ref.17. However, we need to improve our treatment to have some numerical prediction for GdN because it is magnetic and multiple bands are involved. As for the bcc hydrogen [5], we may apply our MIT mechanism. In fact, the variational Monte-Carlo results seems to indicate the weak first-order phase transition [18, 19].

In conclusion, we have given a theoretical analysis for the metal-insulator transition through the band-overlap mechanism. We have showed that it occurs as the first-order phase transition; when the band gap is getting smaller, the insulator phase suddenly changes to the metal phase because of the energy gain due to the Fermi statistics and due to the correlational motion for the Coulomb interaction. In our treatment, the self-consistency in QS\textit{GW} is not fully included; we only consider the rigid shift of energy bands. If we fully include the self-consistency, we should have some deformation of the energy bands (changes of effective masses). However, we expect that our conclusion will be unchanged qualitatively. To treat kinds of materials in practice, it will be necessary to improve our method. Further, we will have to examine roles of other effects like excitonic effects or phonon effects.

This work was supported by ONR contract N00014-7-1-0479. We are also indebted to the Ira A. Fulton High Performance Computing Initiative.

[1] J. N. Huiberts, R. Griessen, H. H. Rector, R. J. Wijngaarden, J. P. Dekker, D. G. de Groot, and N. J. Koeman, Nature (London) 380 (1996).
[2] M. Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. 70, 1039 (1998).
[3] T. Kotani, J.Phys.: Condens. Matter 10, 9241 (1998).
[4] M. Gr"uning, A. Marini, and A. Rubio, The Journal of Chemical Physics 124, 154108 (pages 9) (2006), URL \url{http://link.aip.org/link/?JCP/124/154108/1}.
[5] E. Kioupakis, P. Zhang, M. L. Cohen, and S. G. Louie, Physical Review B
[6] F. Aryasetiawan and O. Gunnarsson, Rep. Prog. Phys 61, 237 (1998).

[7] F. Aryasetiawan and O. Gunnarsson, Phys. Rev. Lett. 74, 3221 (1994).

[8] R. Sakuma, T. Miyake, and F. Aryasetiawan, Physical Review B (Condensed Matter and Materials Physics) 78, 075106 (pages 9) (2008), URL http://link.aps.org/abstract/PRB/v78/e075106.

[9] M. van Schilfgaarde, T. Kotani, and S. Faleev, Phys. Rev. Lett. 96, 226402 (pages 4) (2006), URL http://link.aps.org/abstract/PRL/v96/e226402.

[10] T. Kotani, M. van Schilfgaarde, and S. V. Faleev, Physical Review B (Condensed Matter and Materials Physics) 76, 165106 (pages 24) (2007), URL http://link.aps.org/abstract/PRB/v76/e165106.

[11] S. V. Faleev, M. van Schilfgaarde, and T. Kotani, Phys. Rev. Lett. 93, 126406 (2004).

[12] M. Shishkin, M. Marsman, and G. Kresse, Physical Review Letters 99, 246403 (pages 4) (2007), URL http://link.aps.org/abstract/PRL/v99/e246403.

[13] L. Hedin, Phys. Rev. 139, A796 (1965).

[14] A.L.Fetter and J.D.Walecka, *Quantum Theory of Many-Particle Systems* (McGraw-Hill, New York, 1971).

[15] L. W. S. H. Vosko and M. Nusair, Can. J. Phys. 58, 1200 (1980).

[16] R. Sakuma, T. Kotani, M. van Schilfgaarde, T. Miyake, and S. Tsuneyuki, first-principles study of the pressure-induced insulator-metal transition in YH3.

[17] A. N. Chantis, M. van Schilfgaarde, and T. Kotani, Physical Review B (Condensed Matter and Materials Physics) 76, 165126 (pages 6) (2007), URL http://link.aps.org/abstract/PRB/v76/e165126.

[18] B. G. Pfommer and S. G. Louie, Phys. Rev. B 58, 12680 (1998).

[19] J. Zhu, ph.D. thesis, University of California at Berkeley, 1990.