A remark on the local density approximation with the gradient corrections and the $X_\alpha$ method

Y.-B. Xie, B.-H. Wang, and W.-X. Wang
Department of Modern Physics, University of Science and Technology of China, Hefei, 230026, P.R. China

We report that the solids with narrow valence bands cannot be described by the local density approximation with the gradient corrections in the density functional theory as well as the $X_\alpha$ method. In particular, in the case of completely filled valence bands, the work function is significantly underestimated by these methods for such types of solids. Also, we figured out that these deficiencies cannot be cured by the self-interaction-corrected-local-density-approximation method.

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I. INTRODUCTION

The density functional theory $[1, 2]$ with the generalized gradient approximations $[3, 4]$ (GGA) and the $X_\alpha$ theory $[5, 6]$ have been quite successful in the calculation of various properties in many systems $[7]$, such as the bond length, the bond angle, various properties related to the charge density and the vibration frequencies of many molecules and solids. Moreover, the binding energies of many molecules and the cohesive energies of many solids can be as well roughly evaluated by the GGA and the $X_\alpha$ theory.

Despite those successes, it is also well known $[8]$ that the single particle electronic structure cannot be very well described by the GGA in many solids, since the GGA tends to underestimate the valence band width and the band gap. This is not difficult to understand because even in the electron gas model, the exchange energies for the states far below or far above the Fermi surface are significantly underestimated or overestimated, respectively. Nevertheless, the exchange energy for the states at the Fermi level is correctly given by the GGA for the electron gas case. Therefore, the properties related to the electronic structure at the Fermi surface, for instance, the work function, has been considered correctly explained by the GGA for many solids.

On the other hand, the eigenvalues of the $X_\alpha$ single electron equation cannot be used to estimate the ionization energies of atoms and small molecules. Fortunately, this problem can be cured by introducing the so called transition state method $[5]$.

Let us consider the solids in which the valence electronic states deviates from the plane waves significantly. The electronic properties of this type of solids cannot be described by the electron gas model. In contrast, some characters of the individual atom or small molecular are still kept in such solids. But since the single particle states are quite extended in crystalline solids, the transition state method will no longer be helpful. Hence, a natural question is addressed: can the GGA or the $X_\alpha$ method correctly describe the single particle states near the Fermi surface for such type of solids? We figured out that the answer to this question, unfortunately, is negative from both the academic and practical point of view. Our paper will provide enough evidence to support this conclusion.

In this paper, we study a system composed of spin polarized hydrogen atoms being located on a cubic lattice. The reason to choose such system is for simplicity. Since the spins of all electrons are parallel, the correlation energy is insignificant, and actually is zero in the case of large lattice constant. The exchange energy can be treated exactly by the Hartree Fock method. Also the exchange functional in the GGA and the $X_\alpha$ method is simple and the correlation functional is negligibly small in this system.

In section III, we consider the large $a$ case in which the overlap of the localized hydrogen electron wavefunctions on different sites is negligible. We rigorously show that in GGA or in $X_\alpha$ method, the ionization energy in such case is given by the eigenvalue of the single particle equation for one hydrogen atom which is roughly $[9] 0.29$ and deviates from the exact ionization energy $0.5 - 37/a^4$ considerably (Note that here the term $37/a^4$ is the hole polarization term). This difference, as we can see, is present not only in the spin polarized hydrogen solids, but also in many other systems, where atoms are well separated and the single particle wavefunctions are extended. Notice here that the total bulk energy can still be correctly given by the GGA or the $X_\alpha$ theory.

In section IV, we study the finite $a$ case in which the overlap of the localized wavefunctions on different sites cannot be neglected. In this case, the single particle wavefunctions must be extended. Therefore, similar to the reported results in the last paragraph, we expect that the work function is still significantly underestimated by the GGA or the $X_\alpha$ method when $a$ is not small. This expectation is indeed correct up to $a = 5$ at which the band width is nearly $0.25$. When $a$ is sufficiently small, the single particle states can be characterized by the plane wave and the work function should be correctly predicted by the GGA or the $X_\alpha$ theory.

Finally in section V, we summarize our results.
II. THE MODEL

Let us consider $N$ hydrogen atoms located on a cubic lattice with the lattice constant $a$. For simplicity, we assume that the spins of all electrons are up. In this paper, we study the work function for the $N$ electrons system, i.e., the ground state energy difference between the $N$ electrons system and the $N - 1$ electrons system with fixed $a$.

We investigate this system using the Hartree Fock method and the GGA or the $X_\alpha$ method. The correlation energy is not significant because the spins of the electrons are parallel. Actually, the contribution of the correlation energy is not significant because the spins of the electrons are parallel. Hence, the Hartree Fock method is accurate to predict the work function. On the other hand, the GGA is also quite simple in this case because only the exchange functional is significant whereas the correlation functional is small (In this paper, we shall ignore the correlation functional because it is absent for a single hydrogen atom.). We focus on the error of the work function predicted by the GGA or the $X_\alpha$ method.

When $a$ is finite, the occupied single electron states are described by the Bloch state $|k\rangle = \int d^3r u_k(r)|r\rangle$ with $|k_x|, |k_y|, |k_z| < \pi/a$. In the framework of Hartree Fock theory, $u_k = u_k^{HF}$ satisfy the Hartree Fock equation

$$\sum_p \int d^3r |u_p^{HF}(r')|^2 \frac{u_p^{HF}(r')}{|r - r'|} u_k^{HF}(r) \delta_{p, k} - \sum_p \int d^3r |u_p^{HF}(r')|^2 \frac{u_p^{HF}(r')}{|r - r'|} u_k^{HF}(r) = \epsilon_{HF}(k) u_k^{HF}(r),$$

(1)

(2)

$$U(r) = - \sum_{R_i} \frac{1}{|r - R_i|},$$

(3)

with $R_i$ representing the lattice points. The Hartree Fock orbital energy can be also written as

$$\epsilon_{HF}(k) = \langle k | T + U | k \rangle + \sum_p \langle pp | k k \rangle - \langle pk | kp \rangle$$

(4)

with $T = -\nabla^2/2$ and

$$\langle k_1 k_2 | k_3 k_4 \rangle = \int d^3r \int d^3r' \frac{u_{k_1}^*(r) u_{k_2}^*(r') u_{k_3}(r) u_{k_4}(r')}{|r - r'|}.$$

(5)

Because the Bloch states $|k\rangle$ are extended, the Hartree Fock wavefunctions $u_p(r)$ will be not modified when one electron in $|k\rangle$ is removed. According to the Koopman’s theorem, the ionization potential associated with the state $|k\rangle$ is simply given by $-\epsilon_{HF}(k)$. By adding the correction from the correlation energy, one obtains the exact ionization potential. Since the state at the $X$ point $k = (\pi/a, \pi/a, \pi/a)$ is at the top of the electronic band, the work function is approximately given by $-\epsilon_{HF}(X)$.

In the framework of GGA, $u_k = u_k^{GGA}$ which is determined by the Kohn-Sham equation

$$\frac{1}{2} \nabla^2 + U(r) + \sum_p \int d^3r' \frac{u_p^{GGA}(r')}{|r - r'|} u_p^{GGA}(r)\delta_{p, k} + v_{xc}(n(r)) u_k^{GGA}(r) = \epsilon_{GGA}(k) u_k^{GGA}(r)$$

(6)

with the exchange-correlation potential given by

$$v_{xc}(n(r)) = \frac{\delta E_{xc}[n]}{\delta n(r)},$$

(7)

where $E_{xc}[n]$ is the exchange-correlation functional and

$$n(r) = \sum_p u_p^{GGA}(r) u_p^{GGA}(r).$$

(8)

The total electronic energy of this system is given by

$$E = \sum_k \int d^3r u_k^{GGA}(r)(-\frac{1}{2} \nabla^2) u_k^{GGA}(r) + \int d^3r U(r) n(r) - \frac{1}{2} \int d^3r u_k^{GGA}(r) n(r) u_k^{GGA}(r) + E_{xc}[n] + U_{NN},$$

(9)

where

$$U_{NN} = \sum_{i<j} \frac{1}{|R_i - R_j|}.$$ 

(10)

Next, we consider the $N - 1$ electrons system with the $|k = X\rangle$ state unoccupied. Since $|X\rangle$ is extended, the total electron density $n'(r)$ for the $N - 1$ electrons system is approximately equal to $n(r)$ in the large $N$ limit. Thus the GGA solution $u_k^{GGA}(r)$ is not modified and we self-consistently confirms that $n' \approx n$. The total ground electron energy for the $N - 1$ system is given by

$$E' = \sum_k \int d^3r u_k^{GGA}(r)(-\frac{1}{2} \nabla^2) u_k^{GGA}(r) + \int d^3r U(r) n'(r) - \frac{1}{2} \int d^3r u_k^{GGA}(r) n'(r) u_k^{GGA}(r) + E_{xc}[n'] + U_{NN},$$

(11)

with

$$n_k(r) = u_k^{GGA*}(r) u_k^{GGA}(r).$$

(12)
where $\sum_k$ means the summation over all $k$ states except the $X$ state and $n'(r) = n(r) - n_X(r)$. Since $n_X \ll n$ in the large $N$ limit, we obtain the work function
\[ W = E' - E = -\epsilon^{GGA}(X) \] (14)
which is just the orbital energy of the state $|X>$. Eq.(14) can also be obtained by the transition state method generally used in the $X_\alpha$ method. It is worthwhile to point out that for finite system or when the hole state is localized, Eq.(14) is no longer valid.

From many calculations for atoms and small molecules, we know that the orbital energy obtained in the GGA or the $X_\alpha$ method is significantly lower than the exact ionization potential. Therefore, one suspects that $W$ is significantly underestimated by Eq.(14) in solids in which the valence electrons cannot be described by the plane wave states. In the following sections, this suspicion has been proved to be true.

### III. NON OVERLAPPING CASE

In this section, we study the large $a$ case in which the overlap between the atomic wavefunctions on different sites is negligible. In this case, one can immediately obtain the solution in the Hartree Fock theory and in the GGA or the $X_\alpha$ method. Actually in the Hartree Fock theory, we have
\[ u^{HF}_k(r) = \frac{1}{N} \sum_{R_i} e^{ikR} \phi^{HF}_0(r - R_i) \] (15)
with $\phi^{HF}_0(r)$ being the exact ground state wavefunction for a single hydrogen atom located at $R = 0$, and
\[ \epsilon^{HF}_0(k) = -0.5. \] (16)

Therefore, the work function predicted by the Hartree Fock approximation is $W^{HF} = 0.5$. There is a correction to $W$ from the correlation energy in the $N - 1$ electrons system corresponding to the hole polarization term. The magnitude of this correction is $-37/a^4$ (We have ignore the Van der Waals interaction term which is very small.)

On the other hand, in the GGA or the $X_\alpha$ method, we have
\[ u^{GGA}_k(r) = \frac{1}{N} \sum_{R_i} e^{ikR} \phi^{GGA}_0(r - R_i) \] (17)
with $\phi^{GGA}_0(r)$ being the ground state wavefunction in the GGA or the $X_\alpha$ method for a single hydrogen atom located at $R = 0$ and $\phi^{GGA}_0(r)$ satisfying the following equation
\[ (-\frac{1}{2} \nabla^2 - \frac{1}{r} + \int d^3r' \frac{n_0(r')}{|r - r'|} + v_{xc}(\phi^{GGA}_0)(r))\phi^{GGA}_0(r) = \epsilon^{GGA}_0\phi^{GGA}_0(r), \] (18)

where
\[ n_0^{GGA}(r) = |\phi^{GGA}_0(r)|^2 \] (19)
with
\[ \epsilon^{GGA}_0(k) = \epsilon^{GGA}_0 + \int d^3r \phi^{GGA}_0^*(r)(-\frac{1}{2} \nabla^2)\phi^{GGA}_0(r) \]
\[ + \frac{1}{r} \int d^3r' \frac{n^{GGA}_0(r')}{|r' - r|} + v_{xc}(\phi^{GGA}_0(r))|n^{GGA}_0(r)|, \] (20)

The above equation indicates that the work function $W$ is indeed given by the orbital energy of the single atom in the GGA or the $X_\alpha$ method in this case. However, it is well known that the orbital energy of a single atom in the GGA or the $X_\alpha$ method is much less in magnitude than the corresponding ionization potential. For hydrogen atom, $\epsilon^{GGA}_0$ is found to be $-0.29$ in $X_\alpha$ method, in which $\alpha$ is chosen such that the self interaction energy is exactly canceled by the exchange functional $E_x[n]$ (Note that we have used the exact wavefunction $\phi^{HF}_0(r)$ in Eq.(20) to calculate $\epsilon^{GGA}_0$). The difference between the work function given by the Hartree Fock theory and that given by the $X_\alpha$ method is $(00|00)/3 \approx 0.208$ with
\[ (00|00) = \int d^3r d^3r' \frac{n^{HF}_0(r)n^{HF}_0(r')}{|r - r'|} = 0.625. \] (21)

It should be pointed out that the difference between the exact $\epsilon^{GGA}_0$ evaluated by $\phi^{GGA}_0(r)$ and the above value is insignificant.\[3\] In GGA, the magnitude of $\epsilon^{GGA}_0$ is even less than 0.29. Thus, the work function is remarkably underestimated in this case by the GGA or the $X_\alpha$ method.

We need to point out that the above conclusion is not only applicable to the hypothetic solid in which the spin polarized hydrogen atoms are located on a cubic lattice, but also applicable to the real crystalline solids, with spin up and spin down electrons, satisfying the following two conditions (i) The energy bands are either completely filled or completely empty. (ii) The lattice constant is sufficiently large such that the overlap of the wavefunctions between different lattice sites is negligible. This conclusion can be derived using the exactly same way as for our hypothetic solid. Many real solids for instance, the solids formed by Ne, Ar, Kr, Xe atoms at low temperatures and even ice (Note that there is polarization induced by the dipole moment by the nearby water molecular. But this effect is very small.) may satisfy the above two conditions. It should be noticed that for instance for the Ne solid, the work function is obtained by the Hartree Fock orbital energy together with the corrections from the electron correlation effect as well as the lattice relaxation effect (i.e., the polaron effect). The magnitude of those corrections should be less than 0.1. However, the difference of the orbital energy between the HF theory and the GGA is estimated as 0.4. So the underestimation of the work function for the solid Ne given by the GGA is expected to be quite significant (about 0.3).
Although the ionization potential is remarkably underestimated in the non-overlapping case, the total electronic energy $E$ is still correctly given by the GGA or the $X_\alpha$ method when the band is completely filled. Since

$$n^{\text{GGA}}(r) \approx \sum_{\mathbf{R}_i} n_0^{\text{GGA}}(r - \mathbf{R}_i)$$

(22)

and

$$n_0^{\text{GGA}}(r - \mathbf{R}_i) n_0^{\text{GGA}}(r - \mathbf{R}_j) \approx 0$$

(23)

when $\mathbf{R}_i \neq \mathbf{R}_j$, we have

$$E = N \int d^3r \phi_0^{\text{GGA}}(r) (-\frac{1}{2} \nabla^2) \phi_0^{\text{GGA}}(r)$$

$$+ \left[-\frac{1}{\mathbf{r}} + \frac{1}{2} \int d^3r' \frac{n_0^{\text{GGA}}(r')}{|\mathbf{r} - \mathbf{r}'|} n_0^{\text{GGA}}(r) + E_{xc} [n_0^{\text{GGA}}] \right]$$

$$\approx -0.5N.$$ 

(24)

Since the bandwidth is vanishing in the non-overlapping case, it may be interesting to consider the localized hole state. In this case, the ionization potential equals $0.5 - 37/a^4$ and is correctly given by the GGA or the $X_\alpha$ method. Unfortunately, the GGA predicts that the energy of the extended hole state is lower than the energy of the localized hole state.

It may be pedagogic to discuss the case that the band is only partially filled. Here, for simplicity, we shall only consider the infinite $a$ case. Suppose that there are $Z \leq N$ spin polarized electrons in the system. Assuming that the single particle states are all extended over the whole lattice. In the $X_\alpha$ theory, the total electronic energy is found to be

$$E(Z, N) \approx -\frac{1}{2} Z (1 - \frac{\langle 00|00 \rangle}{2} \frac{Z}{N} - \frac{Z}{N})^2.$$ 

(25)

(Note that this equation is valid only when $\alpha = \infty$. When $a$ is large but finite, there is an additional term $C/a$ for $E(Z, N)$ when $Z \neq N$.) In Eq. (2), we have used $\delta_{HF}(\xi)$ in the construction of Bloch states, where $\xi$ is a variational scaling parameter which is used to minimize the total $X_\alpha$ energy. Therefore, the total electronic energy is significantly overestimated when the band is only partially filled. Interestingly, when $Z \ll N$, one may obtain a lower value for $E(Z, N)$ by assuming all single particle states are extended only over five lattice sites. According to Eq.(25), one may obtain the ionization potential for $Z$ electrons

$$I(Z, N) = E(Z - 1, N) - E(Z, N)$$

$$= \frac{1}{2} \left[ \left(\frac{\langle 00|00 \rangle}{2} \frac{Z}{N} \frac{Z}{N} \right)^{1/3} \right]$$

$$\left[ 1 - \frac{\langle 00|00 \rangle}{2} \left( \frac{5}{3} \frac{Z}{N} \right)^{1/3} \right].$$

(26)

Notice that when the band is half filled $Z = N/2$, we have $I = 0.516$ which is close to the exact value 0.5

It may be necessary to mention that this deficiency in the GGA or the $X_\alpha$ method is also found in some molecular systems at the dissociation limit, such as $H_2^+$, $F_2^+$, NaCl, et.al. Essentially, both failures of the GGA or the $X_\alpha$ method for the solids at large $a$ and for molecules at the dissociation limit are caused by the same reason. The authors in Ref. [10, 11, 12] attributed this type of failure to the so called self-interaction error. However, we deem that this viewpoint is inappropriate because the self-interaction error is zero in our system, yet the magnitude of the total electronic energy is still significantly overestimated by the $X_\alpha$ method. This fact also suggests that the self-interaction-corrected local density approximation method is not helpful to improve the result.

We notice as well that the overestimation of the magnitude of the electronic energy by the $X_\alpha$ method is more pronounced in our system than in diatomic molecular cases, because the electronic states are much more extended in our case. For instance, consider the ionization potential of two spin polarized hydrogen atoms at the fixed separation distance $a$. When $a$ is large and the atomic wavefunction overlap between two hydrogen atoms is negligible small, we can obtain that the error of the ionization potential given by the $X_\alpha$ method

$$
\delta I = \langle 00|00 \rangle \left[ \left(\frac{1}{2} \right)^{4/3} - \frac{1}{4} \right] - \frac{1}{4a}$$

$$\approx 0.092 - \frac{1}{4a},$$

(27)

where the polarization term has been neglected because it is proportional to $1/a^4$. This error is significantly lower than that in solid case. For instance, when $a = 5$, this number is only 0.04 which is much less than 0.21 in the solid case. This fact explains why the GGA or the $X_\alpha$ method are still successful for small molecular near equilibrium geometry.

IV. FINITE OVERLAP CASE

In the last section, we have discussed the large $a$ case in which the overlap of the wavefunctions on different sites is negligible. However, the GGA or the $X_\alpha$ method are usually applied to real solids of finite bandwidth. When $a$ is sufficiently small, the electrons in our system can be described by the plane wave. Therefore, one may speculate that the GGA becomes valid for not large $a$ case in our system. On the other hand, for large $a$, the atomic nature still remains and it can be expected that the error of the work function predicted by the GGA or the $X_\alpha$ method is still significant even when the bandwidth is finite. So it is highly desirable to see how this error decreases when $a$ decreases.

When $a$ is finite and the bandwidth is not zero, it is not easy to calculate the electronic energy accurately even within the framework of the HF theory or the GGA. Instead, we shall take several approximations which can
greatly simplify the calculations.

At first, we assume $u_k^{HF}(r) \approx u_k^{GGA}(r)$ and calculate the difference of the work function predicted by the Hartree Fock theory and the GGA or the $X_\alpha$ method. When the hole state is extended, straightforward calculation yields

$$\Delta W = W_{HF} - W_{GGA} = \Delta_1 - \Delta_2$$

(28)

with

$$\Delta_1 = \sum_k \langle kX|Xk \rangle,$$

(29)

$$\Delta_2 = \int d^3r v_{xc}(n(r))n_X(r),$$

(30)

where $n$ and $n_X$ are the total electron density and the electron density of the state $|X>$, respectively, $W_{HF}$ and $W_{GGA}$ are the work function obtained by the Hartree Fock theory and the GGA, respectively. Note that this assumption has been tested in atomic calculations. The error from this assumption is found to be insignificant.\(^\text{3}\)

Secondly, we assume

$$u_k(r) = \frac{C(k)}{\sqrt{N}} \sum_{R_i} e^{ik \cdot R_i} \phi_0^{HF}(r - R_i)$$

(31)

with the normalization constant

$$C(k) = \frac{1}{\sqrt{\sum_{R_i} S(R_i) e^{ik \cdot R_i}}}$$

(32)

where the overlap is defined as

$$S(R) = \int d^3r \phi_0^{HF}(r) \phi_0^{HF}(r - R)$$

(33)

This assumption is valid in the tight binding limit. While for small $a$ and large bandwidth, different $|k>$ states are made of different $\phi$ and this assumption becomes invalid. However, since both the quantities $\langle kX|Xk \rangle$ and $v_{xc}$ do not depend on $u_k$ sensitively, we expect that this assumption is valid at least when $a$ is not small. Under this assumption, the work function difference $\Delta W$ can be evaluated numerically.

Thirdly, we shall use the $X_\alpha$ exchange functional with the parameter $\alpha = \alpha_1$ selected to cancel the self-interaction exactly in the atomic limit. So we have

$$E_{xc}[n(r)] = \frac{20 \pi^{1/3}}{27} \int d^3r n^{4/3}(r).$$

(34)

Since $\alpha_1$ is greater than the corresponding value in the electron gas model, and furthermore our system will reduce to the electron gas model in the small $a$ limit, we expect that this exchange functional will slightly overestimate the exchange energy in the finite $a$ case. Table I lists the numerical value of $\Delta_1$, $\Delta_2$ and $\Delta W$ for various values of $a$. From this table, one can see that when $a \geq 5$, $\Delta W$ significantly deviates from zero (Note that when $a = 3$ and $a = 4$, we expect that the second approximation becomes invalid. For instance when $a = 4$, the bandwidth is estimated as 0.5 and the electronic states cannot be described by Eq. (31).). Even after subtracting the correction from the correlation energy contribution $37/a^4$, the underestimation of the work function by this $X_\alpha$ method is still about 0.12 at $a = 5$. On the other hand, the band width is about 0.25 when $a = 5$. Therefore, we can conclude that the work function will be underestimated by the $X_\alpha$ method when (i) the valence bands are completely filled and (ii) the bandwidth of the valence bands is not large.

We have also used the generalized gradient approximation exchange functional to calculate $\Delta_2$. In GGA, the exchange functional is expressed as

$$E_{xc}[n] = A \int d^3r n^{4/3} F(t)$$

(35)

with $A = -(3/4)(6/\pi)^{1/3}$,

$$F(t) = (1 + 0.021326t + 0.0037909t^2 + 0.000000891t^3)^{1/15}$$

(36)

and

$$t = \frac{(\nabla n)^2}{n^{8/3}}.$$\(^\text{31}\)

(37)

And $\Delta_2$ is evaluated by

$$\Delta_2 = A \int d^3r \frac{4}{3} n^{1/3} n_X F(t) + F'(t) \left[ 2 \nabla n \cdot \nabla n_X \frac{8}{3} \frac{(\nabla n)^2 n_X}{n^{11/3}} \right].$$

(38)

As expected, $\Delta_2$ evaluated by this formula is indeed slightly less than that by the $X_\alpha$ method. For instance, when $a = 4$, $\Delta_2$ is found to be 0.548 in GGA which is slightly less than the value 0.577 given by $X_\alpha$ method.

V. DISCUSSION

In this paper, we have studied the hypothetic system composed of the hydrogen atoms with spin polarized electrons on a cubic lattice. We found that for the case of narrow bandwidth and completely filled band, the work function is significantly underestimated by the GGA or the $X_\alpha$ method. This is attributed to the significant lower energy of the extended hole state obtained by the GGA or

| $a$ | 3.0 | 4.0 | 5.0 | 6.0 | 7.0 | $\infty$ |
|-----|-----|-----|-----|-----|-----|-----|
| $\Delta_1$ | 0.859 | 0.738 | 0.685 | 0.656 | 0.639 | 0.625 |
| $\Delta_2$ | 0.716 | 0.577 | 0.504 | 0.465 | 0.442 | 0.417 |
| $\Delta W$ | 0.143 | 0.161 | 0.181 | 0.191 | 0.197 | 0.208 |

TABLE I: The calculated results for $\Delta_1$, $\Delta_2$, $\Delta W$ at various values of $a$. |
the Xα method. Note that this problem cannot be cured by assuming that the hole state is localized. Actually, the GGA or the Xα method predicts a significant lower energy for the extended hole state than for the localized hole state even in the zero bandwidth limit.

Although we have only calculated a hypothetic system, our results may lead us to speculate the validity of the GGA or the Xα method in the calculations of the work function of the insulators with narrow valence bands in many ionic crystals, as well as Ne,Ar,Kr,Xe solids (assuming the lattice constant fixed.). Furthermore, it is not difficult to see that the GGA or the Xα method becomes invalid in calculating the ionization potential for the extended, including noncrystalline, systems, where the valence electrons cannot be described by the plane waves. As we have already observed, the GGA or the Xα method would predict that the hole state is extended over many different regions which are distant from each other even in inhomogeneous systems. Such prediction differs from the commonsense.

In section III, we have also pointed out that the magnitude of the total electronic energy is significantly over-estimated by the GGA in the large a limit when the band is not completely filled. Actually, Zhang and Yang and other groups [10, 11, 12] also found that H2+,F2+,NaCl et.al. would not be dissociated correctly in the GGA in the large distance limit. This deficiency is more pronounced in solids because the electronic states are more extended. It should be emphasized that the self-interaction of the electronic states in our system is negligibly small. Therefore, this deficiency cannot be removed by the so called self-interaction-corrected local density approximation method [13, 14].

In summary, we speculate that the exact exchange-correlation functional is highly nonlocal when the electron density n(r) varies in space and the system is extended in the density functional theory [1]. When the density of the valence electrons varies greatly in space and the system is extended, the GGA and the Xα method may be unsuitable to describe the system properly.

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