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Band-structure calculations of noble-gas and alkali halide solids using accurate Kohn-Sham potentials with self-interaction correction

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The optimized-effective-potential (OEP) method and a method developed recently by Krieger, Li, and Iafrate (KLI) are applied to the band-structure calculations of noble-gas and alkali halide solids employing the self-interaction-corrected (SIC) local-spin-density (LSD) approximation for the exchange-correlation energy functional. The resulting band gaps from both calculations are found to be in fair agreement with the experimental values. The discrepancies are typically within a few percent with results that are nearly the same as those of previously published orbital-dependent multipotential SIC calculations, whereas the LSD results underestimate the band gaps by as much as 40%. As in the LSD—and it is believed to be the case even for the exact Kohn-Sham potential—both the OEP and KLI predict valence-band widths which are narrower than those of experiment. In all cases, the KLI method yields essentially the same results as the OEP.

I. INTRODUCTION

In the exact Kohn-Sham (KS)[1] density-functional theory (DFT), the exchange-correlation potential, $V_{\text{xc}}^{\text{KS}}(\mathbf{r})$, which is the functional derivative of the exchange-correlation energy functional $E_{\text{xc}}[n]$, $V_{\text{xc}}^{\text{KS}}(\mathbf{r})=\delta E_{\text{xc}}[n]/\delta n$, is strictly self-interaction free,[2] i.e., the self-exchange-correlation interaction is exactly canceled by its counterpart, the self-Coulomb term in the Hartree potential. However, such cancellation is incomplete in the local-density approximation (LDA). As a consequence, many of the properties of atoms, molecules, and solids are not well described. In particular, the underestimate of the band gap for insulating solids has been attributed partially to this failure;[2] i.e., the spurious self-interaction is a positive quantity which raises the energy of electron states unequally, with the more localized highest valence state having a larger change than that of the bottom of the conduction state, resulting in a smaller energy band gap.

Attempts to correct this error using the self-interaction-corrected local-spin-density approximation (SICLSD, or simply SIC) have been made in the past few years with considerable success.[3–5] In all cases, most of the discrepancies due to LDA disappear, with the new result agreeing with experimental values fairly well. However, all the calculations reported have involved the use of the SIC multipotential method, which, although still lying within the framework of the Hohenberg-Kohn[6] density-functional theory, does not belong to the KS prescription. In particular, due to its multipotential nature, an intrinsic shortcoming exists in SICLSD such that it yields orbitals that are not orthogonal unless off-diagonal Lagrange multipliers are introduced which then significantly increases the numerical work.

The question thus raised is the following: If the exact KS exchange-correlation potential $V_{\text{xc}}^{\text{KS}}(\mathbf{r})$ exists, will it be able to account accurately for the band gap of insulating solids; and can one actually find a practical $V_{\text{xc}}(\mathbf{r})$ that is applicable to solids?

The first part of the question has been addressed extensively recently.[7–11] With the discovery of the physical significance of the highest occupied eigenvalue of the KS theory,[12] it is now known[7–11] that the exact KS exchange-correlation potential should show an integer discontinuity. That is, when the number of electrons of a system with a discontinuity in the eigenvalue spectrum changes from N to $N+\delta$ (with N being an integer and δ a positive infinitesimal), the $V_{\rm xc}^{N+\delta}(\mathbf{r})$ will jump from $V_{\rm xc}^{N}(\mathbf{r})$ by a constant. For insulating solids, this implies essentially that electrons in the valence and conduction bands will be acted upon by two KS potentials (corresponding to the ground states of N-electron and $N+\delta$-electron systems, respectively), with a nonzero constant difference. It follows, therefore, that for any approximate KS potential (even a very accurate one in terms of its description of the ground-state properties), as long as it fails to show the integer discontinuity, it will fail to predict correctly the band-gap value. (Progress[7–11] has been made in the past in calculating this constant and accounting accurately for the band gap; most of this, however, has used the much more involved self-energy formalism.) LDA is a continuous function of density, and so it cannot have the property of integer discontinuity. Thus LDA does not yield the correct values for the band gaps of the insulating solids.

From these analyses, it thus appears that the answer to the second part of the question is as follows: one has to find an approximate $V_{\rm xc}^{\rm KS}(\mathbf{r})$ which is self-interaction-free and satisfies the integer discontinuity criterion. (It should be noted that the SIC formalism essentially embeds both of these properties. As it is constructed, the SIC is certainly self-interaction-free, and in addition, the electron states in the conduction and valence bands have actually been calculated by using different exchange-correlation potentials.)

In this work, we will show how one could apply the optimized effective potential[13–15] (OEP) method and the method derived recently by Krieger, Li, and Iafrate[16] (KLI) to the band-structure calculations of insulating solids. The $V_{\rm xc}(\mathbf{r})$ of these two methods has the virtue that it satisfies both of the criteria discussed above. We will then present our results and compare with those of LDA and other calculations as well as to experimental results.

II. FORMALISM

As discussed earlier, the unknown exact $V_{\rm xc}^{\rm KS}(\mathbf{r})$ is self-interaction-free and possesses the property of integer discontinuity. The LDA and those approximations with gradient expansion corrections, however, satisfy neither of these two conditions. Currently, there is no known $V_{\rm xc}$ which is a functional of density only and which respects the integer discontinuity criterion. In fact, whether one can ever find such $V_{\rm xc}$ has been questioned.[11]

However, if one constructs an exchange-correlation energy functional that is orbital dependent, $E_{\rm xc}=E_{\rm xc}[\phi_i]$ like that of Hartree-Fock (HF) or SIC, then although in general one can still not find its functional derivative with respect to the density (which is $V_{\rm xc}$) analytically, since $\phi_i=\phi_i[n]$ is not known, one can always solve for this $V_{\rm xc}$ numerically by using the OEP[13–15] method, i.e., given

$$\begin{aligned} E&=E[\phi_i]\\ &=T[\phi_i]+E_H[n]+E_{\rm xc}[\phi_i]+\int d\mathbf{r}\, v_{\rm ext}(\mathbf{r})n(\mathbf{r}) ,\\ T[\phi_i]&=\sum_i \langle \phi_i^*|-\tfrac{1}{2}\nabla^2|\phi_i\rangle , \\ E_H[n]&=\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\frac{n(\mathbf{r}')n(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} , \end{aligned} \tag{1}$$

where $\{\phi_i,\ i=1,2,\ldots,N\}$ are eigenfunctions of a single local effective potential $V^{\rm OEP}$,

$$h^{\rm OEP}\phi_i=(-\tfrac{1}{2}\nabla^2+V^{\rm OEP})\phi_i=\varepsilon_i\phi_i , \tag{2}$$

with $V^{\rm OEP}$ being determined by requiring that $E[\phi_i]$ is minimized for all $\{\phi_i\}$ obtained from Eq. (2). This results in

$$\begin{aligned} \frac{\delta E}{\delta V}&=\sum_i\int\frac{\delta E}{\delta\phi_i^*(\mathbf{r}')}\frac{\delta\phi_i^*(\mathbf{r}')}{\delta V(\mathbf{r})}d\mathbf{r}'+{\rm c.c.}\\ &=\sum_i\int\frac{\delta\phi_i^*(\mathbf{r}')}{\delta V(\mathbf{r})}h_i\phi_i(\mathbf{r}')d\mathbf{r}'+{\rm c.c.}=0 , \end{aligned} \tag{3}$$

where h_i is given by

$$h_i\phi_i(\mathbf{r})=\frac{\delta E}{\delta\phi_i^*(\mathbf{r})} \tag{4}$$

and is the single-particle Hamiltonian for orbital i and $\delta\phi_i/\delta V$ can be calculated by using the Green's function:

$$\begin{aligned} \frac{\delta\phi_i(\mathbf{r}')}{\delta V(\mathbf{r})}&=-G_i(\mathbf{r}',\mathbf{r})\phi_i(\mathbf{r}) ,\\ (h^{\rm OEP}-\varepsilon_i)G_i(\mathbf{r},\mathbf{r}')&=\delta(\mathbf{r}-\mathbf{r}')-\phi_i(\mathbf{r})\phi_i^*(\mathbf{r}') . \end{aligned} \tag{5}$$

With the application of Eq. (2) and rearrangements, one finally obtains an integral equation for the effective exchange-correlation potential $V_{\rm xc}(\mathbf{r})$:

$$\int H(\mathbf{r},\mathbf{r}')V_{\rm xc}(r')d\mathbf{r}'=Q(\mathbf{r}) , \tag{6}$$

$$\begin{aligned} V_{\rm xc}(\mathbf{r})&=V^{\rm OEP}-\left[-\frac{Z}{r}+\int d\mathbf{r}'\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\right] ,\\ H(\mathbf{r},\mathbf{r}')&=\sum_i\phi_i^*(\mathbf{r})G_i(\mathbf{r},\mathbf{r}')\phi_i(\mathbf{r}') ,\\ Q(\mathbf{r})&=-\sum_i\int d\mathbf{r}'\phi_i^*(\mathbf{r})G_i(\mathbf{r},\mathbf{r}')v_{\rm xc}^i(\mathbf{r}')\phi_i(\mathbf{r}') , \end{aligned} \tag{7}$$

and

$$v_{\rm xc}^i(\mathbf{r})=\frac{\delta E_{\rm xc}[\phi_i]}{\phi_i\delta\phi_i^*} , \tag{8}$$

which corresponds to the effective exchange-correlation orbital-dependent potential in the HF or SIC formalism.

It has been pointed out[17] that when this formalism is applied to the HF energy functional, the effective exchange potential is exactly the KS exchange potential in the exchange-only theory.

Talman and Shadwick[14] have performed the OEP-HF (referred to as the optimized potential model or OPM by them) calculations and found that in all cases the OEP-HF yields total energies that are very close to the corresponding HF values. Applying this method to the SICLSD energy functional, Norman and Koelling[15] obtained a local orbital-independent exchange-correlation potential, which by the same argument should be regarded as the KS potential for this SICLSD energy functional; and found that it gives nearly the same results as the multipotential SICLSD calculations for both the total energy and the eigenvalue of the highest occupied state.

It follows from their constructions that both OEP-HF and OEP-SIC are self-interaction-free. In addition, they also display the property of integer discontinuity. Norman and Koelling have demonstrated in their application of OEP-SIC the discontinuous jump of the $\mathrm{Li}^{0.02-}$ spin-down potential.[15] A similar jump, which is essentially a constant, also appears for the OEP-HF.[18]

The major problem with the OEP method is its complexity in the numerical programming. Great care needs to be taken to ensure an accurate calculation of the single-particle energy eigenvalues.[19,20]

Recently, after analyzing the OEP integral equation, KLI derived an approximate solution for the OEP equation;[16] i.e., they found an analytic expression for the $V_{\mathrm{xc}}(\mathbf{r})$ for the exchange-correlation energy functional $E_{\mathrm{xc}}=E_{\mathrm{xc}}[\phi_i]$, which for a spin-unpolarized system may be written

$$V_{\mathrm{xc}}(\mathbf{r})=\sum_i \frac{n_i(\mathbf{r})v^i_{\mathrm{xc}}(\mathbf{r})}{n(\mathbf{r})}+\sum_i \frac{n_i(\mathbf{r})}{n(\mathbf{r})}(\bar{V}^i_{\mathrm{xc}}-\bar{v}^i_{\mathrm{xc}}) , \tag{9}$$

where $n_i(\mathbf{r})$ is the orbital density, $n_i(\mathbf{r})=|\phi_i(\mathbf{r})|^2$, and $n(\mathbf{r})=\sum_i n_i(\mathbf{r})$. $\bar{V}^i_{\mathrm{xc}}$ and $\bar{v}^i_{\mathrm{xc}}$ are the expectation values of $V_{\mathrm{xc}}(\mathbf{r})$ and $v^i_{\mathrm{xc}}(\mathbf{r})$ with respect to orbital i. $\bar{V}^i_{\mathrm{xc}}$ may be determined by solving a matrix of the order of the number of nondegenerate orbitals. The first term is essentially the exact Slater potential[21] when $E[\phi_i]=E_{\mathrm{HF}}[\phi_i]$, and is a weighted averaged SIC potential as suggested by Perdew and Zunger[2] if SIC energy functional is assumed.

Atomic calculations[16,19,22] show that in all situations, the KLI potential mimics the OEP results extremely well, and even correctly preserves the property of integer discontinuity both qualitatively and quantitatively. In addition, it yields total energies that are only a third of the difference of the OEP and HF results (the typical OEP results are only a few ppm above that of HF), and are closer to the HF or OEP-HF than those given by the method developed recently by Harbola and Sahni.[23] Moreover, the KLI method is also very easy to program and the eigenvalues thus obtained are very stable and reliable (being only a few parts per thousand from the OEP-HF results).

Applications of both OEP and KLI to atoms have been very successful. In these applications, they are also easier to implement, since one needs only deal with localized states. It will be much more involved if one attempts to apply the OEP or the KLI method to solids. For one thing, the SIC approach is reasonable only when applied to localized orbitals like Wannier states.

However, for solids like noble gases and some of the alkali halides like NaCl which have very localized charge density around each atom or ion site, one can still apply OEP or KLI approximately by employing the linear augmented plane-wave (LAPW) method using the atomiclike wave functions assuming integer atomic occupation numbers within each muffin-tin sphere. The error thus introduced will be small, since the charge density for these systems leaks outside the muffin-tin sphere by only a few hundredths of electrons.

For simplicity, in our calculations, we have applied the OEP and KLI to the SIC functional suggested by Perdew and Zunger.[2] The $v^i_{\mathrm{xc}}(\mathbf{r})$ in Eq. (8) then assumes the form

$$v^i_{\mathrm{xc}}(\mathbf{r})=V^{\mathrm{LSD}}_{\mathrm{xc}}[\tfrac{1}{2}n,\tfrac{1}{2}n] - \left[V^{LSD}_{\mathrm{xc}}[n_i,0]+\int d\mathbf{r}'\frac{n_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\right] , \tag{10}$$

where $V^{\mathrm{LSD}}_{\mathrm{xc}}[n_\uparrow,n_\downarrow]$ is the LSD exchange-correlation potential.

Solving for $V_{\mathrm{xc}}(\mathbf{r})$ from Eq. (6) or Eq. (9), one can then use either result instead of the commonly used LDA for the exchange-correlation potential in the LAPW band-structure calculation.

In this work, we have approximated the exchange-correlation potential by the OEP or KLI solution only inside the muffin-tin sphere, the usual LDA approximation is employed in the interstitial region where electron charge density is both low and extended.

It should be noted that the $V_{\mathrm{xc}}(\mathbf{r})$ of OEP or KLI thus constructed is an approximate KS potential which is expected to result in accurate calculations of only ground-state properties; i.e., only electron properties in the valence band might be appropriately described. The energy band gap between the valence and conduction bands may be obtained by imagining that a single electron is added to the system so that the conduction-band minimum is occupied. We treat this conduction state as extended, so that its effect on the electron density of the system is negligible. The new $V_{\mathrm{xc}}(\mathbf{r})$ has a discontinuous jump from the $V_{\mathrm{xc}}(\mathbf{r})$ which governs the behavior of the electrons in the valence bands.

In our calculations, we used LDA (as has been done in other SIC-type calculations), to compute the energy states in the conduction band. This is a one-shot calculation which employs the converged OEP or KLI self-consistently determined electron densities. We have also made direct calculations of the conduction states; in this case all energy levels are calculated using the OEP or KLI $V_{\mathrm{xc}}(\mathbf{r})$ that was used to calculate the valence-band states.

III. RESULTS

Employing the OEP and KLI methods, we have performed the band-structure calculations for the noble-gas solids Ne, Ar, Kr, and Xe and an alkali halide, NaCl. The calculations were performed by using a LAPW code. All relativistic effects have been included except the spin-orbit coupling. The lattice parameters used are 8.435, 10.05, 10.66, and 11.59 a.u. for Ne, Ar, Kr, and Xe, respectively, and 10.658 a.u. for NaCl. For noble-gas solids, we use the touching sphere model in determining the muffin-tin radius. For NaCl, we use the same parameters as used by Norman and Perdew.[5]

In the following, we present the results for the band gaps as well as intraband transitions in the valence band from X_4' to Γ_{15} and from L_2' to Γ_{15}. For noble-gas solids, the latter determines the valence-band (VB) width, whereas for NaCl, the experimental result is available only for the X_4' to Γ_{15} transition. We will mainly concentrate on the discussion of the calculated results for band gaps. At the end of the section, we will also briefly discuss the results for the conduction levels.

A. Band gap

1. *Exchange plus correlation*

Table I lists the results for the band gaps and the two valence intraband transitions. In all cases, except for the HFC calculation, the von Barth and Hedin[24] correlation expression has been used. Besides OEP and KLI, we have also quoted the Hartree-Fock plus correlation (HFC),[25,26] SIC,[4,5] and experimental results[27,30] wherever available. For comparison, the results of our LDA calculations are also presented, which are essentially equivalent to those previously published.[5,31,32]

From the table, we can see that the OEP and KLI band gaps agree with the experimental results fairly well for all the noble-gas and NaCl solids. Most of the underestimates by LDA have been corrected. In addition, we also notice that these calculations give results which are close to the corresponding multipotential SIC calculations. A similar feature has been found in atomic calculations for the highest occupied eigenvalues, although here we are dealing with the difference of two quantities. Furthermore, as expected, the KLI approximates the exact OEP results very well. For Ne, Ar, and NaCl, the two differ by less than 0.1 eV. For Kr and Xe, the difference increases to about half an electron volt. Moreover, we observe that the KLI gaps are always less than the experi-

TABLE I. Band-gap and valence-band width. All calculations except HFC have employed the von Barth–Hedin correlation. Energies are in electron volts. Experimental band gaps for noble-gas solids are from Ref. 27, and bandwidths from Ref. 28. HFC results for rare gas are from Ref. 25, and NaCl from Ref. 26. The numbers in parentheses are the gaps calculated using OEP or KLI method neglecting the integer discontinuity effect.

	Expt.	LDA	OEP	KLI	SIC	HFC
			Noble gas			
			Ne			
Γ_1^c-Γ_{15}^v gap	21.4	11.5	20.9 (15.2)	20.8 (15.2)	20.2[a]	22.2
Γ_{15}-X_4' width		0.63	0.48	0.48		0.3
Γ_{15}-L_2' width	1–1.3	0.70	0.52	0.53	0.59[a]	0.4
			Ar			
Γ_1^c-Γ_{15}^v gap	14.2	8.2	13.1 (9.7)	13.1 (9.7)	13.5[b]	15.2
Γ_{15}-X_4' width		1.17	1.07	1.07		1.0
Γ_{15}-L_2' width	1.7	1.30	1.17	1.16	1.21[b]	1.2
			Kr			
Γ_1^c-Γ_{15}^v gap	11.6	6.8	11.1 (8.0)	10.8 (7.9)		13.6
Γ_{15}-X_4' width		1.41	1.31	1.32		1.2
Γ_{15}-L_2' width	2.3	1.56	1.42	1.43		1.4
			Xe			
Γ_1^c-Γ_{15}^v gap	9.8	5.8	9.5 (6.9)	9.0 (6.7)		
Γ_{15}-X_4' width		1.49	1.50	1.53		
Γ_{15}-L_2' width	3.0	1.76	1.62	1.65		
			Alkali halide			
			NaCl			
Γ_1^c-Γ_{15}^v gap	9.0[c]	5.5	9.5 (6.3)	9.5 (6.4)	9.2[a]	10.0
Γ_{15}-X_4' width	2.4±0.2[d]	1.74	1.43	1.42	1.80[a]	3.0
Γ_{15}-L_2' width		2.01	1.75	1.73	1.93[a]	2.4

[a] Reference 5 (a simplified SIC has been used rather than that of Ref. 2).

[b] Reference 4.

[c] Reference 29.

[d] Reference 30.

mental values for the noble-gas solids, whereas it is just the contrary for the NaCl. This might be attributed, at least partially, to the approximation made in the construction of the KLI potential if we recall that the V_{xc} of OEP or KLI inside each muffin-tin sphere is calculated from all the occupied states of the individual atom or ion. In both the noble-gas and NaCl solids, the lowest conduction band is formed from the atomic s state and the valence band is formed from the atomic p states. However, whereas in the noble-gas solids, the s and p states that formed the two bands are from the same atom, they are from different ions in NaCl.

Inside the parentheses next to the OEP and KLI band-gap values, we also list for each method the band gaps calculated entirely by using the same potential (OEP or KLI) which was used to calculate the valence and core states. That is, one neglects the property of the KS potential, which should have a discontinuous jump for calculating the energy eigenvalue for an electron in the bottom of the conduction band. As expected, the band gap thus calculated is not wide enough to account for the experiment. For example, for neon, whereas the correct treatments of the OEP and KLI give 20.9 and 20.8 eV, respectively, in close agreement with the experimental result of 21.4 eV, the incorrect direct calculations yield only 15.2 eV in both cases. If we regard the OEP and KLI as an accurate KS potential, we then see that the discontinuity constant is about 6 eV for neon. On the other hand, it is also worth noting that these direct gaps are, nevertheless, larger than those given by LDA and correct about a third of the LDA underestimate. This can be attributed to the fact that the $V_{\mathrm{xc}}(\mathbf{r})$ of OEP or KLI is self-interaction-free.

2. *Exchange-only case*

In LDA calculations, the exclusion of the correlation effect narrows the band gap by a few tenths of an electron volt. On the contrary, as can be seen from Tables I and II, with the application of SIC, the band gaps increase by about half an electron volt when the effect of correlation is neglected. The increase of the band gap in LDA calculation is understandable when one realizes that the LDA correlation potential lowered the energy levels of the more localized valence band more than those in the conduction band. In OEP and KLI, however, the contribution from the self-interaction-corrected term for the correlation for these solids is a positive quantity which is also weighted more for the valence states, so neglecting correlation in these potentials has the opposite effect on

TABLE II. Band gap and valence-band width for noble-gas and alkali halide solids in an exchange-only calculation. Same notation as Table I.

	Expt.	LDA	OEP	KLI	SIC	HF
			Noble gas			
			Ne			
Γ_1^c-Γ_{15}^v gap	21.4	10.8	21.3 (15.1)	21.1 (15.0)		25.1
Γ_{15}-X_4' width		0.67	0.49	0.49		0.3
Γ_{15}-L_2' width	1–1.3	0.75	0.53	0.54		0.4
			Ar			
Γ_1^c-Γ_{15}^v gap	14.2	7.7	13.6 (9.6)	13.7 (9.7)	13.9[a]	18.5
Γ_{15}-X_4' width		1.24	1.09	1.08		1.1
Γ_{15}-L_2' width	1.7	1.38	1.19	1.18	1.23[a]	1.3
			Kr			
Γ_1^c-Γ_{15}^v gap	11.6	6.4	11.7 (8.0)	11.4 (7.9)		16.5
Γ_{15}-X_4' width		1.49	1.33	1.34		1.4
Γ_{15}-L_2' width	2.3	1.64	1.44	1.45		1.6
			Xe			
Γ_1^c-Γ_{15}^v gap	9.3	5.5	10.0 (6.9)	9.6 (6.7)		
Γ_{15}-X_4' width		1.69	1.51	1.54		
Γ_{15}-L_2' width	3.0	1.86	1.64	1.67		
			Alkali halide			
			NaCl			
Γ_1^c-Γ_{15}^v gap	9.0[b]	5.3	10.1 (6.5)	10.1 (6.5)		15.9
Γ_{15}-X_4' width	2.4±0.2[c]	1.81	1.41	1.40		3.4
Γ_{15}-L_2' width		2.10	1.72	1.71		2.7

[a] Reference 4.

[b] Reference 29.

[c] Reference 30.

the band gap calculation.

It is interesting to note that the direct calculation of the band gaps using OEP and KLI method are almost unchanged with or without correlation, i.e., the application of the SIC correlation merely shifts the energy levels (both valence and conduction states) by nearly a constant. The difference is only of the order of 0.01 eV. It thus appears that the OEP or KLI correlation potential makes nearly an equal contribution to the conduction- and valence-band states.

Finally, we note here that unlike the OEP and KLI, the reported HF and HFC band gaps differ by as much as 3–6 eV. This is because in HFC calculation, a different form of correlation has been used (i.e., the electron polaron model). It is expected that calculations using the HF method with the von Barth–Hedin correlation will have a much smaller difference than those of the HF and HFC, as found in our OEP and KLI results.

B. Bandwidth

Compared with experiment, LDA gives valence bands which are too narrow for both the noble-gas solids and NaCl. Application of the self-interaction correction does not improve the results and in fact, the bandwidths become slightly narrower.[5] Calculation by Kunz[26] using HFC method predicts 3.0 eV for VB from (X'_4 to Γ_{15}) for NaCl, in agreement with the experimental value of 3.0 eV given by Pong and Smith.[33] However, it is not clear where such transition occurs in the experiment. In fact, Himpsel and Steinmann[30] reported an experimental result of 2.4 eV for transition from X'_4 to Γ_{15}. Examining the results for NaCl in Table I, it is seen that the HFC method produces a relative position for states of X'_4 and L'_2 that are different from the density functional results. The HFC, however, predicts the same relative position of X'_4 and L'_2 for all the noble-gas solids as the density-functional methods. Our OEP and KLI methods yield the narrowest VB among the density-functional methods, but not by a significant amount. The relative position of the states studied is the same as the other DFT calculations. The reason that the OEP and KLI predict a narrow VB is simply that the KS formalism will only describe the highest occupied state correctly. All states lower than the top of the valence band will be raised and all unoccupied states will be lowered if the same potential is used. It is also interesting to observe, from the results in Tables I and II, that the valence intraband transition widths are nearly independent of the effect of correlation for the OEP or KLI calculations. The difference is typically of the order of 0.01 eV. This, once again, demonstrates that the correlation effect plays a very minor role in the description of the large band-gap solids. Notice, for LDA, the influence of correlation is nearly an order of magnitude larger than that of OEP or KLI.

C. Conduction levels

It is well known[34] that LDA yields conduction levels that are too compressed. Since in our calculations, we have in fact used LDA (but using OEP or KLI density) in calculating these levels, it is thus expected that we will obtain results that follow the same pattern for the conduction levels as LDA. This is exactly the case. For example, for NaCl, LDA gives 5.3, 1.9, 2.1, and 5.8 eV (relative to the conduction level bottom of Γ_1) at Γ'_{25}, X_1, X_3, and X'_4 points, respectively, compared with 5.1, 1.9, 2.1, and 5.9 eV of OEP and 5.2, 1.9, 2.1, and 5.9 of KLI (the reported experimental results by Himpsel and Steinmann[30] give 8.2±0.2, 2.4±0.5, 3.0±0.5, and 8.0±0.5 eV, respectively). For neon (at the same four points), LDA yields 17.9, 6.8, 11.3, and 12.4 eV, OEP gives 17.8, 6.8, 11.1, and 12.4 eV, and KLI predicts 17.8, 6.8, 11.1, and 12.6 eV.

However, the "direct" calculation of these states, i.e., calculation using the same V_{xc} of OEP or KLI that was used to calculate the valence and core levels, predicts conduction-band levels that are significantly different from those of LDA. In this case, for example, we obtain, at the same four points: Γ'_{25}, X_1, X_3, and X'_4, 5.4, 0.64, 3.0, and 6.5 eV for NaCl crystal in both OEP and KLI calculations. The 0.64 eV at X_1 is significantly different from the 1.9 eV of LDA. For Ne, we have 16.8, 7.3, 11.1, and 14.9 eV for both OEP and KLI, which are also very different from those of LDA.

IV. CONCLUSION

In this work we have shown how the OEP method can be applied approximately to the SIC exchange-correlation energy functional for insulating solids. In addition, we have also shown how accurate the KLI method mimics the OEP in all the calculations. Just as in the atomic case, the two methods yield essentially equivalent results. As a consequence, we have actually demonstrated how one can calculate the band gaps accurately by using accurate KS exchange-correlation potential like OEP or KLI without relying upon the more involved self-energy formalism. From this study, it is also found that both OEP and KLI methods produce results (at least for the band gap and the width of the valence band) that are quite close to those of the multipotential SIC results.

Most remarkable about these two exchange-correlation potentials is that they are both self-interaction-free and possess the property of integer discontinuity. From earlier analysis and our results, it has now become clear that respecting these two properties is essential for any approximate KS potential to account accurately for the band gaps of insulating solids.

Since, as is well known,[7–12] the KS theory will only give an exact result for the highest occupied energy eigenvalue, therefore, except for the calculation of the band gap, states in other parts of the calculated band structure using the KS (even the exact KS) method will in general not have the desired accuracy as one might expect. In other words, it is the intrinsic nature of the KS theory that it will yield in general a too narrow valence band and too compressed conduction bands, and such behavior will be particularly magnified when dealing with insulating solids with a large band gap, since in this case, the KS potential will underestimate the self-interactions of the valence states other than the highest energy state and raises their energy. Our calculations using both OEP and KLI V_{xc} confirm the above statements in all respects: the band gaps are in good agreement with experiment, the valence-band widths and relative conduction-band levels are all significantly different from the experimental values.

This, however, does not mean that the KS method should not be utilized in band-structure calculations. The usefulness of it is evidenced by its success in the description of metals.[35] Even for insulating solids, due to its simplicity of being a single potential, which automatically guarantees the orthogonality of the calculated orbitals, it might still be desirable to calculate the band structure using the KS method, and then simply add on a single-shot correction to all states, similar to those performed by Perdew and Norman[36] in correcting the LDA eigenvalues.

Finally, we point out that although in this work we have been able to perform both the OEP and KLI calculations, approximations have been made such that in fact only those solids which have large electron charge densities around each ion or atom (i.e., interstitial charge density is small) could be described accurately. In addition, the treatment of the conduction band by LDA might not be as accurate, especially for semiconductors which have small gaps. A better approximation would be to derive directly from the OEP equation or the KLI construction the appropriate value of the integer discontinuity as has been done for atoms.[16,22] Due to its numerical complexity, the OEP method might not be easy to apply to other solids like semiconductors, because it will not be possible to solve the OEP integral equation for a potential using an atomiclike approximation. For these cases, due to its relative simplicity and the fact that the potential is given as an explicit functional of the occupied orbitals, the KLI method might be easier to apply.

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