PHYSICAL REVIEW B VOLUME 28, NUMBER 4 15 AUGUST 1983

Simplified self-interaction correction applied to the energy bands of neon and sodium chloride

Michael R. Norman
Department of Physics and Quantum Theory Group, Tulane University, New Orleans, Louisiana 70118

John P. Perdew
Department of Physics and Quantum Theory Group, Tulane University, New Orleans, Louisiana 70118
and Institute for Theoretical Physics, University of California, Santa Barbara, California 93106

(Received 27 April 1983)

The local-density approximation (LDA) for the exchange-correlation potential underestimates the fundamental energy gaps of insulators by about 40%. When a simplified self-interaction correction (SSIC) is applied to the band structures of Ne and NaCl, vast improvements over LDA are found in the gaps, with little change in the valence-band widths or conduction-band structures. Because it is applied directly to the Bloch orbital representation, SSIC is very easy to incorporate into LDA computer codes. Results are also reported using the Langreth-Mehl (LM) generalized gradient correction to LDA. The LM potential, which we regard as a close approximation to the exact Kohn-Sham potential, yields band structures very close to those of LDA.

I. INTRODUCTION

Self-consistent-field calculations within the local-density approximation[1] (LDA) for the exchange-correlation potential yield a set of orbital energies ϵ_α. Unfortunately, $-\epsilon_\alpha$ cannot usually be identified with the energy needed to remove an electron from orbital $\psi_\alpha(\vec{r})$ (as measured by photoemission, for example.) One of the reasons this is so is that the LDA one-electron effective potential contains a spurious interaction of each electron with itself. This spurious piece has been subtracted out[2] and the resulting potential applied with success to self-consistent calculations for atoms. In particular, the physical removal energies of the electrons (including even intra-atomic relaxation effects) are approximated by the self-interaction—corrected orbital energy eigenvalues.[2]

Direct application of the self-interaction correction (SIC) to extended systems like crystals poses severe problems. The energy-minimizing solutions of the SIC one-electron equations are usually *localized* orbitals,[2] which of course maximize that fraction of the exchange energy which is self-exchange (treated exactly in SIC). No band structure results.

Nevertheless, there have been several successful attempts to implement SIC in band-structure calculations. Zunger[3] constructed an SIC periodic potential for the valence band of solid argon by using a localized valence orbital density renormalized to the unit cell. Heaton, Harrison, and Lin[4] used optimized Wannier-type orbitals in calculations for argon and lithium chloride. By either method, the ~40% error of the LDA band gap is dramatically reduced, as expected from atomic estimates[2] and from the pioneering LiF study of Zunger and Freeman.[5]

We have recently proposed a method[6] of our own for the implementation of an approximate self-interaction correction to the LDA orbital energies. Unlike the methods described above, our simplified self-interaction correction (SSIC) does not require the construction of localized orbitals. Consequently, it is very easy to incorporate into existing LDA codes.

In SSIC, we simulate the self-interaction correction to the LDA potential by addition of a local, energy-dependent term[6]

$$\Delta v_{\mathrm{xc}}(\vec{r},\epsilon)=-0.104\frac{\hat{u}\cdot\vec{\nabla}\rho(\vec{r},\epsilon)}{\rho(\vec{r},\epsilon)} \tag{1}$$

(in hartrees). Here $\rho(\vec{r},\epsilon)$ is the local density of states,

$$\rho(\vec{r},\epsilon)=2\sum_{\alpha}|\psi_\alpha(\vec{r})|^2\delta(\epsilon-\epsilon_\alpha)\ , \tag{2}$$

and $\hat{u}$ is a unit vector in the direction of the gradient of the total electron density

$$n(\vec{r})=\int_{-\infty}^{\mu}d\epsilon\,\rho(\vec{r},\epsilon)\ . \tag{3}$$

Fundamentally, an electronic exchange potential is an in-

TABLE I. Xenon atom. Orbital energies $-\epsilon_\alpha$ compared to measured electron removal energies (hartrees). Energies averaged over magnetic subshells. LDA: local-density approximation; SIC: original self-interaction correction; SSIC: simplified self-interaction correction; Expt.: experiment.

α	LDA	SIC	SSIC	Expt.[a]
1s	1254.8	1271.6	1267.3	1270.2
2s	195.5	198.4	198.4	200.4
2p	175.7	179.5	178.4	179.7
3s	40.0	41.0	41.0	42.2
3p	33.6	34.7	34.6	35.2
3d	24.0	25.3	24.9	25.0
4s	7.2	7.7	7.6	8.0
4p	5.2	5.6	5.6	5.8
4d	2.19	2.57	2.51	2.51
5s	0.73	0.90	0.89	0.86
5p	0.31	0.45	0.43	0.46

[a] Reference 7.

verse length, and the length choosen in Eq. (1) is the localization length for electrons of orbital energy ϵ. [Of course, more complicated forms may be constructed for the right-hand side of Eq. (1), to make more limits right.]

In an atom, the correction (1) is roughly constant over the radial extent of the orbitals of energy ϵ. As a result, the correction may be applied as a first-order perturbation upon the LDA orbital energies. The resulting SSIC orbital energies for both core and valence electrons agree closely with the original SIC orbital energies[2] and with measured removal energies,[7] as we showed in Ref. 6. Table I shows typical results for the xenon atom from that work (but not published before).

Equation (1) is size consistent, and in a crystal it makes a contribution to the periodic one-electron potential. The localization length now roughly describes the pileup around the nuclei of the Bloch orbital densities at energy ϵ.

For crystalline core or atomic electrons, $\rho(\vec r,\epsilon)$ in Eq. (1) may be replaced by the spherical average of the orbital density at energy ϵ. But for crystalline valence electrons, the construction of $\rho(\vec r,\epsilon)$ is tedious, and we choose to replace $\rho(\vec r,\epsilon)$ in Eq. (1) by the valence electron density,

$$\rho_{\mathrm{val}}(\vec r)=\int_{\epsilon_0}^{\mu} d\epsilon\,\rho(\vec r,\epsilon)\ , \tag{4}$$

where ϵ_0 is the bottom of the valence band. (Note that a similar equal-weight average over the valence band occurs in the construction of a Wannier orbital from Bloch orbitals.) For the unoccupied or conduction bands, we take $\Delta v_{\mathrm{xc}}(\vec r,\epsilon)=0$, for reasons discussed in previous work.[2-4]

Finally, we observe that while Eq. (1) is approximately constant over space for an atomic orbital, it must vanish on the surface of the unit cell in a crystal. [Figure 1 shows Eq. (1) evaluated for the $2p$ valence electrons in atomic versus crystalline neon.] For this reason, we report both perturbative and self-consistent SSIC calculations for crystals. The latter involve the self-consistent solution of

$$\left[-\tfrac{1}{2}\nabla^2+v(\vec r)+\int d^3r'\,\frac{n(r')}{|\vec r-\vec r'|}+v_{\mathrm{xc}}^{\mathrm{LDA}}(\vec r)+\Delta v_{\mathrm{xc}}(\vec r,\epsilon_\alpha)\right]\psi_\alpha(\vec r)=\epsilon_\alpha\psi_\alpha(\vec r) \tag{5}$$

[where $v(\vec r)$ is the electron-nuclear potential] along with Eqs. (1)–(4). We have found that it makes no difference to the valence and conduction bands whether the core orbitals are constructed self-consistently in LDA or SSIC, at least for systems like Ne where the core orbitals are energetically deep. [We actually use semirelativistic generalizations of Eqs. (2) and (5), as described in the next section.]

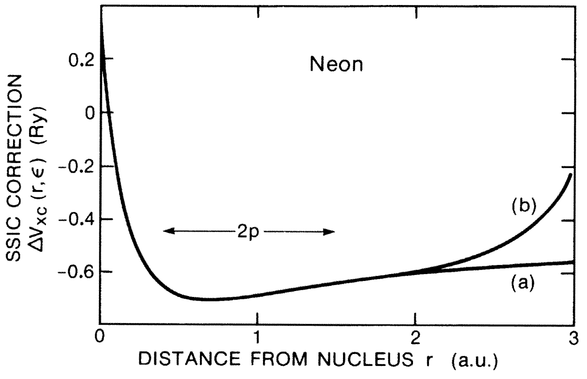

FIG. 1. Simplified self-interaction correction [Eq. (1)] to the one-electron potential seen by the $2p$ valence electrons in (a) atomic and (b) crystalline neon (rydbergs). The muffin-tin radius is 2.98 bohr. The horizontal arrows display the radial extent of the $2p$ orbital, $\langle r\rangle \pm (\langle r^2\rangle - \langle r\rangle^2)^{1/2}$, in the atom.

II. NUMERICAL PROCEDURES

We use a linear—augmented-plane-wave (LAPW) code[8] kindly provided by Dale Koelling. All relativistic effects other than spin-orbit splitting are included, as is correlation in the parametrization of von Barth and Hedin.[9] The self-consistent potential is sphericalized inside each muffin-tin sphere, but has an unconstrained shape in the interstitial region (the warped muffin-tin approximation[10]).

The chosen lattice constants are (in bohrs) 8.435 (Ne) and 10.658 (NaCl). In Ne, the muffin-tin spheres just touch. In NaCl, their radii, 2.207 (Na) and 3.068 (Cl), have been chosen after examination of measured electron density maps.[11] (In fact, NaCl has been chosen as our alkali halide example because the Na atom is much more spherical than the Li atom in the lithium halides.) The numbers of plane-wave basis functions at Γ are 59 (Ne) and 89 (NaCl), corresponding to $KR=8$ and 7, respectively, where K is the length of the greatest reciprocal-lattice vector and R is the average muffin-tin radius. The LAPW "energy parameters" are optimized for valence and conduction levels separately.

III. RESULTS

Here we report the results of our calculations for the fundamental energy gap (conduction-band bottom minus valence-band top) and valence-band width in Ne (Table II) and NaCl (Table III), plus certain conduction levels in NaCl (Table IV).

A. Experimental values

For neon, Rössler[12] reports a band gap of 21.4 eV. Photoelectron energy distributions measured by Schwentner *et al.*[13] suggest that the band width is about 1.3 eV but might be as small as 1.0 eV.

For sodium chloride, optical reflectance measurements by Roessler and Walker[14] reveal a band gap of 9.0 eV. Himpsel and Steinmann,[15] using angle-resolved photoemission have found the bandwidth to be approximately 2.4 eV. These authors[15] have also measured the conduction-band structure at Γ and X.

B. Local-density approximation

Our LDA results for the band gap and bandwidth agree reasonably well with earlier LDA exchange-only ($X\alpha=\frac{2}{3}$) calculations.[16,17] The previous LDA results we quote for Ne have been scaled to our lattice constant by Trickey, from the calculations in Ref. 16. The APW calculation of Melvin and Smith[17] for NaCl is not self-consistent.

In comparison with experiment, our LDA results exhib-

TABLE II. Neon crystal. Band gap and valence-band width (eV). LM: Langreth-Mehl gradient approximation; HF: Hartree-Fock; HFC: Hartree-Fock plus correlation corrections. Pert. denotes perturbative and SC denotes self-consistent calculations.

		LDA		SSIC				
	Expt.	Previous[a]	Present	Pert.	SC	LM	HF[b]	HFC[b]
Gap $\Gamma_1^c-\Gamma_{15}^v$	21.4[c]	11.2	11.5	19.6	20.2	12.7	25.1	22.2
Width $\Gamma_{15}-L_2'$	1-1.3[d]	0.7	0.70	0.58	0.59	0.62	0.4	0.4

[a] Reference 16.
[b] Reference 23.
[c] Reference 12.
[d] Reference 13.

it the expected[2,18] trends: The band gap is about 40% too small, and the valence band is somewhat too narrow. Furthermore, the conduction bands, measured from the conduction-band bottom, are much too compressed.

C. Simplified self-interaction correction

As a first test of SSIC for neon, we compare self-consistent SSIC with Zunger's cellular SIC method.[3] Since there are less than 0.04 electrons in the interstitial region, the SSIC and SIC contributions from the interstitial region are neglected. The resulting SSIC gap, 19.83 eV, is extremely close to the cellular SIC value, 19.73 eV. The corresponding bandwidths, 0.57 and 0.54 eV, are also close.

The SSIC results reported in Tables II–IV include the interstitial correction. Note that while there is not much difference between perturbative (pert.) and self-consistent (SC) SSIC, the self-consistent results are always slightly better in comparison with experiment.

Compared to the LDA values, the SSIC band gaps are much wider (and stand in very good agreement with experiment), while the SSIC valence bands are slightly narrower. Heaton, Harrison, and Lin[4] have found very similar corrections to LDA in Ar and LiCl, using their Wannier-orbital SIC method.

The narrowing of the valence band which occurs under SSIC is not hard to understand: The Γ_{15} state at the top of the valence band is more localized, and hence sees larger gradients, than the L_2' state at the bottom of the band.

Finally, we consider the NaCl conduction levels. Recall that the conduction states see no direct SSIC correction to the LDA potential. Nevertheless, they see an indirect effect due to changes in the valence electron density. As a result, the SSIC conduction band, measured from the conduction-band bottom, is slightly stretched out in comparison with the LDA conduction band. This stretching goes in the right direction, but not nearly far enough, to agree with experiment.

D. Langreth-Mehl generalized gradient correction

The Langreth-Mehl[19,20] (LM) correction to the LDA potential reduces to the bare gradient correction for slowly varying densities $n(\vec{r})$, but purges certain spurious contributions[21] which arise for realistic density variations and which have in the past given gradient expansions a bad reputation. There is now ample evidence from atomic studies[20] that the LM correction significantly reduces the small errors of the LDA electron density and total energy.

Because of numerical problems with higher-order gradients of the very low interstitial density, we have included the Ne calculation. The LM interstitial correction has, however, been included for NaCl. Note that, like SSIC, however been included for NaCl. Note that, like SSIC, LM slightly narrows the valence band (because LM provides a higher potential barrier around each atom). There is also an increase over LDA in the band gap, but the increase due to LM correction is only slight. We suspect that the serious underestimation of the band gap which occurs in LDA and LM is a feature of the unknown exact Kohn-Sham[1] potential (that local, energy-independent potential which regenerates the exact density when applied to a system of noninteracting electrons).

The LM inhomogeneity correction does increase the neon band gap slightly, by 1.2 eV above the LDA value. It may be noted that when this correction is added to the SSIC band gap of 20.2 eV, the result is 21.4 eV, in agreement with the measured value. For a study of the effects of LM correction on the band structure and Fermi surface of a metal, see Ref. 22.

TABLE III. Sodium chloride crystal. Band gap and valence-band width (eV).

		LDA		SSIC				
	Expt.	Previous[a]	Present	Pert.	SC	LM	HF[b]	HFC[b]
Gap $\Gamma_1^c-\Gamma_{15}^v$	9.0[c]	5.1	5.6	9.3	9.2	6.0	15.9	10.0
Width $\Gamma_{15}-X_4'$	2.4±0.2[d]	1.6	1.77	1.78	1.80	1.75	3.4	3.0
$\Gamma_{15}-L_2'$			2.03	1.88	1.93	1.98	2.7	2.4

[a] Reference 17.
[b] Reference 24.
[c] Reference 14.
[d] Reference 15.

TABLE IV. Sodium chloride crystal. Conduction levels, measured from the conduction-band bottom (eV).

State	Expt.[a]	LDA	SSIC SC	LM	HF[b]	HFC[c]
Γ_1	0	0	0	0	0	0
Γ_{25}'	8.2±0.2	5.1	5.3	4.9	8.0	7.3
X_1	2.4±0.5	1.8	2.0	1.7	3.0	2.6
X_3	3.0±0.5	1.9	2.2	1.9	3.3	3.1
X_4'	8.0±0.5	5.6	5.7	5.5	7.7	8.7

[a] Reference 15.
[b] Reference 25.
[c] Reference 24.

E. Hartree-Fock and extensions

Hartree-Fock (HF) calculations have been performed for Ne by Kunz and Mickish[23] and for NaCl by Kunz.[24] These authors have also included certain correlation corrections (HFC), e.g., via the electronic polaron model. For completeness, we have also included their results in Tables II–IV.

As is well known, the HF gaps are too large, but the correlation corrections bring them into good agreement with experiment. In Ne, the HF and HFC valence-band widths are far narrower than the experimental or even the LDA widths, while in NaCl the HF and HFC valence bands are somewhat too wide. In the valence band of NaCl, the lowest state is at point X in Kunz's HF and HFC calculations, while it is at point L in our LDA and SSIC calculations.

For the conduction levels in NaCl, measured from the bottom of the the conduction band, the HF (Ref. 25) and HFC (Ref. 24) results agree well with experiment, in contrast to the LDA and SSIC bands which are too compressed. Apparently a truly nonlocal potential is needed to get the correct conduction-state energies.

IV. CONCLUSIONS

Before stating our conclusions, we would like to review some exact theorems on electron removal energies from the ground state of any system with fixed nuclei. The LDA effective one-electron potential $v_{\rm eff}^{\rm LDA}(\vec{r})$ is, of course, only an approximation, valid for slowly varying densities $n(\vec{r})$, to the exact Kohn-Sham[1] potential $v_{\rm eff}(\vec{r})$. The latter potential is a functional derivative with the following property: When the derivative is evaluated for infinitesimal density variations $\delta n(\vec{r})$ such that $\int d^3r\,\delta n(\vec{r})<0$, the resulting potential has a greatest occupied orbital energy $\epsilon_{\rm max}$ such that $-\epsilon_{\rm max}$ is the removal energy of the least-bound electron.[26] The other Kohn-Sham orbital energies have no exact physical meaning, as we have shown in Ref. 6. The other electron removal energies have to be found from the complex, nonlocal, and energy-dependent self-energy[27–29] $\Sigma(\vec{r},\vec{r}\,',\epsilon)$.

Real systems, built up from atoms, do not have slowly varying electron densities. As a result, in LDA one finds the $-\epsilon_{\rm max}$ is not (except in metals) a good approximation to the removal energy of the least-bound electron. This discrepancy is strongly reduced by SIC.[2] As a bonus, one finds that the resulting SIC potential (which is local but orbital dependent) seems to be a good approximation to the real part of the self-energy in atoms. Although SIC has been criticized for its use of an orbital- or energy-dependent potential, it is precisely this feature which makes it possible for the SIC orbital energies to approximate *all* of the electron removal energies in an atom.

We suspect, in fact, that the unknown exact Kohn-Sham[1] potential $v_{\rm eff}(\vec{r})$ would yield an insulator band structure with errors similar to those of the local density or Langreth-Mehl[19,20] approximations: a band gap that is much too narrow, a valence bandwidth that is also too narrow, and conduction bands, measured from the conduction-band bottom, that are much too compressed. For the valence-band width at least, the close agreement between LDA and exact Kohn-Sham values follows from our earlier conclusion[6] that LDA orbital energy *differences* between occupied orbitals agree closely with the corresponding exact Kohn-Sham values.

In order to do SIC band-structure calculations entirely within the Bloch orbital representation, we have proposed[6] the simplified self-interaction correction (SSIC) of Eq. (1). We have found that it faithfully mimics SIC corrections to the energies of the atomic orbitals, and we have applied it here to the band structures of Ne and NaCl. Our results are in accord with those found for Ar and LiCl by Heaton, Harrison, and Lin[4] using a completely different implementation of SIC: Vast improvements over LDA are found for the band gaps, but not for the valence-band widths. There is also little improvement over LDA in the conduction-band structure, measured from the conduction-band bottom. We suspect that a fully nonlocal potential (in the sense that Hartree-Fock is nonlocal) is needed to account for the valence-band width and conduction-band structure. However, we believe that SSIC may still serve as a useful spectroscopic potential for atoms and insulators, and possibly for other systems as well.

ACKNOWLEDGMENTS

We thank Dale Koelling for the LAPW codes and instruction in their use. We are also grateful for helpful discussions or correspondence with Dave Langreth, Chun Lin, Gary McPherson, Francesco Sacchetti, John Smith, Sam Trickey, and Alex Zunger, and for support by the National Science Foundation, Grants Nos. DMR-80-16117 and PHY-77-27084.

---

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

[2] J. P. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981), and earlier references therein. Also M. R. Norman (in press).

[3] A. Zunger, unpublished calculation discussed in Ref. 2.

[4] R. A. Heaton, J. G. Harrison, and C. C. Lin, Solid State Commun. 41, 827 (1982), and unpublished.

[5] A. Zunger and A. J. Freeman, Phys. Rev. B 16, 2901 (1977).

[6] J. P. Perdew and M. R. Norman, Phys. Rev. B 26, 5445 (1982).

[7] K. D. Sevier, At. Data Nucl. Data Tables 24, 323 (1979).

[8] D. D. Koelling and G. O. Arbman, J. Phys. F. 5, 2041 (1975); A. H. MacDonald, W. E. Pickett, and D. D. Koelling, J. Phys. C 13, 2675 (1980).

[9] U. von Barth and L. Hedin, J. Phys. C 5, 1629 (1972).

[10] D. D. Koelling, Phys. Rev. 188, 1049 (1969); N. Elyashar and D. D. Koelling, Phys. Rev. B 13, 5362 (1976).

[11] H. Schoknect, Z. Phys. Chem. 3, 296 (1955).

[12] U. Rössler, in *Rare Gas Solids,* edited by M. L. Klein and J. A. Venables (Academic, New York, 1975), pp. 505 and 545.

[13] N. Schwentner, F.-J. Himpsel, V. Saile, M. Skibowski, W. Steinmann, and E. E. Koch, Phys. Rev. Lett. 34, 528 (1975).

[14] D. M. Roessler and W. C. Walker, Phys. Rev. 166, 599 (1968).

[15] F.-J. Himpsel and W. Steinmann, Phys. Rev. B 17, 2537 (1978).

[16] A. K. Ray and S. B. Trickey, Phys. Rev. B 24, 1751 (1981).

[17] J. S. Melvin and T. Smith, Phys. Status Solidi B 49, 173 (1972).

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

[19] D. C. Langreth and M. J. Mehl, Phys. Rev. Lett. 47, 446 (1981).

[20] D. C. Langreth and M. J. Mehl, Phys. Rev. B (in press).

[21] D. C. Langreth and J. P. Perdew, Phys. Rev. B 21, 5469 (1980).

[22] M. Norman and D. D. Koelling Phys. Rev. B (in press).

[23] A. B. Kunz and D. J. Mickish, Phys. Rev. B 8, 779 (1973).

[24] A. B. Kunz, Phys. Rev. B 26, 2056 (1982).

[25] N. O. Lipari and A. B. Kunz, Phys. Rev. B 3, 491 (1971).

[26] J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz, Phys. Rev. Lett. 49, 1691 (1982).

[27] A. H. MacDonald, M. W. C. Dharma-Wardana, and D.J.W. Geldart, J. Phys. F 10, 1719 (1980).

[28] F. Sacchetti, J. Phys. F 12, 281 (1982).

[29] G. Strinati, H. J. Mattausch, and W. Hanke, Phys. Rev. B 25, 2867 (1982).