PHYSICAL REVIEW B **69**, 045111 (2004)

Exact-exchange density-functional calculations for noble-gas solids

R. J. Magyar,[1] A. Fleszar,[2] and E. K. U. Gross[1]

[1]*Theoretische Physik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany*

[2]*Theoretische Physik I, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany*

(Received 30 July 2003; revised manuscript received 4 November 2003; published 29 January 2004)

The electronic structure of noble-gas solids is calculated within density-functional theory's exact-exchange method (EXX) and compared with the results from the local-density approximation (LDA). It is shown that the EXX method does not reproduce the fundamental energy gaps as well as has been reported for semiconductors. However, the EXX-Kohn-Sham energy gaps for these materials reproduce about 80% of the experimental optical gaps. The structural properties of noble-gas solids are described by the EXX method as poorly as by the LDA one. This is due to missing van der Waals interactions in both, LDA and EXX functionals.

DOI: 10.1103/PhysRevB.69.045111 PACS number(s): 71.10.−w, 71.20.Nr

I. INTRODUCTION

Density-functional theory (DFT) is nowadays by far the most popular *ab initio* method to calculate ground-state properties of atoms, molecules, and solids.[1–3] Its generalization to time-dependent phenomena[4] extended the scope of applied DFT to electronic excitations. DFT's successes rely on a construction of accurate and practical approximations to the exchange-correlation part of the energy functional. The local-density approximation (LDA) proposed at the very beginning of DFT[1,2] was and remains a simple tool to use, whose accuracy, however, is surprisingly good given the simplicity of the approximation. Over the years, LDA has been applied to practically all systems of interest. In most cases, LDA describes ground-state properties, such as equilibrium structures, adiabatic phonons, to mention only a few, surprisingly well, even for materials with strongly inhomogeneous electron densities. On the other hand, attempts to describe energy gaps E_g or electronic excitations brought rather limited success.

The case of E_g is a special one because E_g is defined as the difference between the ionization potential I and electron affinity A. Hence, E_g can be written in terms of total ground-state energies of systems with different number of electrons, and it is in principle a ground-state property

$$E_g = I - A = E[N+1] + E[N-1] - 2E[N]. \tag{1}$$

Here $E[N+1]$, $E[N]$, and $E[N-1]$ are the total ground-state energies of the systems with $N+1$, N, and $N-1$ electrons, respectively. It has been shown[5,6] that E_g can be reexpressed in the following form:

$$E_g = E_g^{KS} + \Delta_{xc}, \tag{2}$$

where

$$E_g^{KS} = \epsilon_{N+1}(N) - \epsilon_N(N), \tag{3}$$

is the Kohn-Sham (KS) gap and Δ_{xc} is the discontinuity in the exchange-correlation potential under adding and subtracting an infinitesimal fraction ω of the integer particle number N:

$$\Delta_{xc} = \lim_{\omega \to 0} \left\{ \frac{\delta E_{xc}[n]}{\delta n}\bigg|_{N+\omega} - \frac{\delta E_{xc}[n]}{\delta n}\bigg|_{N-\omega} \right\}_{n_N}. \tag{4}$$

Applying LDA to calculate E_g from Eq. (1), one faces the basic problem that LDA does not bind the $N+1$ atomic electron system. On the other hand, using Eq. (2) within LDA results in the equality of the LDA KS gap and the fundamental gap since the discontinuity Δ_{xc} vanishes in this approximation. As is well known, the LDA-KS absolute gap is always much smaller than the experimental gap, in some cases, it is even qualitatively wrong. Namely, LDA predicts zero gap, a metal, where in nature the system is a semiconductor.

A most interesting development in density-functional theory during last few years was the application of the exact-exchange KS method (EXX) to the case of crystalline solids. For this method, the total-energy functional is given by

$$E[n] = T_S[n] + \int n(r)V_{ext}(r) + \frac{1}{2}\int\int \frac{n(r)n(r')}{|r-r'|} + E_X[n] + E_C[n], \tag{5}$$

where

$$E_X[n] = -\frac{1}{2}\sum_{kk'}^{occ} \int\int \frac{\phi_k^*(r)\phi_k(r')\phi_{k'}(r)\phi_{k'}^*(r')}{|r-r'|} \tag{6}$$

is the exact-exchange energy functional. $T_S[n]$ is the kinetic-energy term of noninteracting electrons and the correlation-energy term $E_C[n]$ remains to be approximated, for example, by LDA. The orbitals ϕ_k in the expression for E_X are KS orbitals, i.e., the orbitals which minimize $T_S[n]$ for a given density $n(r)$ and are therefore functionals of the electron density. For this reason, T_S and E_X are both implicit functionals of the density $n(r)$ and the KS equations can be derived

$$\left(-\frac{1}{2m}\nabla^2 + V_{ext}(r) + V_H[n](r) + V_X[n](r) + V_C[n](r)\right)\phi_k(r) = E_k\phi_k(r), \tag{7}$$

where the KS exchange potential $V_X[n](r) = \delta E_X[n]/\delta n(r)$ is obtained by the chain-rule differentiation

$$V_X(r) = \frac{\delta E_X[n]}{\delta n(r)} = \sum_k^{occ} \int \int \left[\frac{\delta E_X[n]}{\delta \phi_k(r')} \frac{\delta \phi_k(r')}{\delta V_{KS}(r'')} + \text{c.c.} \right] \frac{\delta V_{KS}(r'')}{\delta n(r)}. \tag{8}$$

Here $V_{KS}[n](r)$ is the total KS potential corresponding to the density $n(r)$. Neglecting correlation, the total-energy functional has apparently the form of a Hartree-Fock expression for the total energy. However, the EXX method and the Hartree-Fock method differ because the Hartree-Fock and KS orbitals ϕ_k are not the same. In the Hartree-Fock method these orbitals obey an equation with a nonlocal potential (the Fock operator), whereas in the KS method they are determined by a KS Hamiltonian with a local, multiplicative potential.

For more than two decades, the EXX method, sometimes under the name *optimized effective potential* (OEP), has been applied to atoms and molecules.[7,8] Total ground-state energies were always found to be extremely close to the Hartree-Fock values while the single-particle spectrum—yielding, e.g., a Rydberg series for finite systems—is strongly improved over Hartree-Fock. Only recently, however, has this method been applied to bulk semiconductors, insulators, and metals.[9–15] A surprising result of EXX calculations for sp semiconductors is that the KS energy gaps between occupied and unoccupied states are very close to experimental gaps. This contrasts typical LDA results in which the gaps are always too small. In the EXX case, a larger gap than in LDA is to be expected because the EXX potential is self-interaction free and, thus, binds more strongly than the LDA potential. For example, the EXX-KS electron binding energies in atoms are greater in magnitude than their LDA counterparts and closer to experiment. Since the occupied valence states generally have a greater self-interaction contribution than the more delocalized unoccupied states, the EXX-KS gap should widen as compared to LDA. If the fundamental gap is evaluated from Eq. (1) with total energies in Hartree-Fock approximation, one obtains

$$E_g^{HF} = \epsilon_{N+1}^{HF}(N) - \epsilon_N^{HF}(N). \tag{9}$$

Evaluating, on the other hand, the gap in EXX, Eqs. (2) and (3) yield

$$E_g^{EXX} = \epsilon_{N+1}^{EXX\text{-}KS}(N) - \epsilon_N^{EXX\text{-}KS}(N) + \Delta_x, \tag{10}$$

where Δ_x is the X-only discontinuity. Assuming that, like for finite systems, the total energies in Hartree-Fock and the total energies in EXX are very close, one would expect that Eqs. (9) and (10) yield very similar values for the band gap. This is indeed the case.[13] What is surprising and still not well understood is why the EXX-KS gaps alone, i.e., without adding the discontinuity, are so close to the experimental gaps for sp semiconductors. The prevailing belief is that the *exact* KS gaps are smaller than the true gaps for solids. As there are no exact KS potentials for solids available, this belief is yet unverified. It is not known how large the discontinuity Δ_{xc} given by Eq. (4), of the *exact* exchange-correlation density-functional is. In any case, the EXX method is the only KS method so far yielding the electronic structure close to experiment, provided one ignores the discontinuity which should in principle be considered. This success has some important practical consequences. One of them is the possibility of using the one-electron energy spectrum as a first, approximate description of excitations and as a fast tool to interpret experiments. Another, perhaps more important, is a better starting point for more accurate calculations of excitations via the time-dependent density-functional theory.

In this paper, we explore the performance of the EXX method for materials very different from sp semiconductors, namely, the crystalline noble gases. Solid Ne, Ar, Kr, and Xe are special systems since these materials are composed of almost independent atoms. In fact, the shape of the charge density of superimposed isolated atoms is rather similar to the charge density of the solid and we might expect the energetics to be similar as well. The individual tightly bound close-shell atoms bind very weakly with one another. Therefore these systems are a difficult case for LDA. Indeed, as will be seen in Table IV, the LDA description of the equilibrium structural properties for these solids is much less satisfactory than usual. These solids are large-gap insulators with their experimental energy gaps ranging between 21.4 eV for neon and 9.8 eV for xenon. Furthermore, they have a large exciton binding energy on the order of several eV. Since the noble-gas solids are a loosely bound ensemble of atoms, a comparison between various electronic properties in the solid phase and in isolated atoms is meaningful and interesting. We will investigate both cases within the LDA and EXX methods. As will be seen later, in the atomic case the EXX without correlation resembles highly accurate Kohn-Sham results when they are available. Adding LDA correlation to the exact-exchange potential usually worsens the quality of results. However, for the physical quantities involving total-energies differences, an account of correlation seems to be necessary.

Our results show that the EXX approximation, with and without LDA correlation, widens the LDA Kohn-Sham gaps of noble-gas solids by about 1.3–3.4 eV. However, the KS energy gaps are not as close to the experimental gaps as reported for sp semiconductors. Along with previous observations that the EXX-KS gaps for diamond[13] and MgO (Ref. 9) are smaller than experimental gaps, our results suggest that, at least for large-gap insulators, the EXX theory does not perform as well as it does for sp semiconductors.

It has been suggested that for atoms the exact KS gap between the highest occupied and the lowest unoccupied state represents an approximation of the *optical* gap rather than quasiparticle gap.[16,17] The latter represents a non-neutral excitation or a total-energy difference between the N and $N \pm 1$ particle systems, and the former is the gap between the ground and excited states of the N-electron system. This conjecture has been explicitly verified in the cases where the *almost exact* Kohn-Sham atomic potentials have been calculated.[16,17] Our EXX results for noble-gas atoms (Sec. II) support this conjecture as well. In regard to the solids, the picture is not as clear. For semiconductors the exciton binding energy is very small, of the order of meV, the observed agreement between the EXX-KS gaps and experimental gaps could support the conjecture of Refs. 16,17 as well. However, unless better approximations to the correlation-energy functional are known this remains as a rather inconclusive speculation. Our results for noble-gas solids, systems where optical and quasiparticle gaps differ by several eV and where electronic structure in the solid phase is similar to the structure of energy levels in isolated atoms, could throw some light on the validity of this conjecture. What we have found is that the EXX gaps for noble-gas solids are—unlike the case of semiconductors—significantly smaller than the quasiparticle gaps. However, they are also smaller than the experimental optical gaps, reproducing about 80% of their values. A fundamental question remains then: would an *exact* treatment of correlation align the KS and optical gaps for noble-gas solids as well, or does correlation in the solid phase have a qualitatively different character and role then for finite, atomic systems, so that the conjecture of Refs. 16 and 17 is not correct for solids?

The following section is devoted to results for isolated atoms. Electronic properties of the noble-gas solids are presented and discussed in Sec. III.

II. NOBLE-GAS ATOMS: Ne, Ar, Kr, AND Xe

Since noble-gas solids consist of loosely bound individual atoms, it is instructive to start the investigation by analyzing the properties of isolated atoms. In addition, the density-functional methods for atoms are more advanced than in extended systems and can be used as a test for various approximations. This is for two reasons. First, highly accurate KS potentials are available for a few light atoms like Ne (Refs. 18,19) and Ar.[19] Second, for finite systems it is computationally feasible to calculate the fundamental gap, Eq. (1), from total-energy differences. Note that for finite systems, the fundamental gap as given by Eq. (1) is usually called the chemical hardness. For simplicity, we keep the term ''fundamental gap'' for both finite and infinite systems. In the following we present several results for the noble-gas atoms and draw some conclusions about the validity of certain approximations.

In Tables I and II we present the KS eigenvalues for the Ne and the Ar atom, respectively. Results using LDA, pure EXX (EXX), EXX plus LDA correlation (EXXc), and highly accurate (almost exact) KS potentials for Ne and Ar atoms are presented. The column denoted QMC in Table I shows eigenvalues resulting from the KS potential obtained by Umrigar and Gonze[18] through a quantum Monte Carlo calculation of the ground-state density of the Ne atom. The column denoted CI in Tables I and II shows the results obtained by Morrison and Zhao[20] from highly accurate densities which were calculated through the configuration-interaction approach. The column called Expt. contains the negative of the experimental first ionization potential of each atom which should be compared to the uppermost occupied KS eigenvalue. The column also contains the experimental binding energies of a few excited states. The latter are defined as the negative of the difference between the experimental ionization potential and the experimental optical energy gap between the ground state and the relevant excited state. For the optical gap we take a weighted average of singlet and triplet gaps. As for the occupied levels, we report only the experimental ionization potential, i.e., the binding energy of the highest occupied state. This is because it is unclear how the lower KS eigenvalues compare with the physical binding energies. However, for unoccupied states, it has been suggested that the KS eigenvalues are a good approximation to the experimental binding energies of the excited atoms.[16,17] This idea has been explicitly verified for helium,[16] beryllium,[16] and neon atoms;[17] some plausible arguments have been put forward to explain why.[16]

TABLE I. Neon-atom energy levels (in eV). The Kohn-Sham energies are from LDA, exact exchange (EXX), and exact exchange with LDA correlation (EXXc). Column QMC gives the eigenvalues obtained with the almost exact Kohn-Sham potential of Ref. 18. Column CI presents results of almost exact Kohn-Sham calculation of Ref. 20.

Ne	LDA	EXX	EXXc	QMC	CI	Expt.
$1s$	−824.34	−838.30	−840.38	−838.18	−838.30	
$2s$	−35.97	−46.73	−48.40	−44.93	−45.01	
$2p$	−13.54	−23.14	−24.76	−21.61	−21.69	−21.56
$3s$	−0.07	−5.23	−5.77	−4.97		−4.9
$3p$		−3.11	−3.40	−3.00		−2.94
$4s$		−1.95	−2.03	−1.90		−1.89
$3d$		−1.57	−1.63	−1.55		−1.53

Tables I and II show that LDA KS eigenvalues are smaller in magnitude than their EXX and EXXc counterparts. The magnitude is largely a consequence of the self-interaction error inherent in the LDA method. Another consequence of this self-interaction error in LDA is the absence of none higher but the first bound, unoccupied state. These facts are well known. What is more interesting for this study is that EXX eigenvalues for Ne and Ar are deeper than the exact ones. This means that the EXX method binds atomic states of Ne and Ar too strongly and exact correlation would cor-

TABLE II. Argon-atom energy levels (in eV). The Kohn-Sham energies are from LDA, exact exchange (EXX), and exact exchange with LDA correlation. Column CI presents results of almost exact Kohn-Sham calculation of Ref. 20.

Ar	LDA	EXX	EXXc	CI	Expt.
$1s$	−3095.39	−3112.99	−3115.42	−3113.82	
$2s$	−293.61	−303.27	−305.13	−302.59	
$2p$	−229.67	−237.46	−239.36	−236.85	
$3s$	−24.02	−29.90	−31.37	−28.79	
$3p$	−10.40	−16.07	−17.48	−14.88	−15.76
$4s$	−0.26	−4.37	−4.94		−4.08
$4p$		−2.77	−3.09		−2.66
$3d$		−1.86	−2.29		−1.83

rect for this overbinding. When LDA correlation are added to the exact exchange (EXXc method) the situation worsens. For example, the EXX uppermost occupied eigenvalues are roughly 1.5, 0.3 eV deeper than the exact eigenvalues for Ne and Ar, respectively. In the EXXc method the difference grows to 3.2 and 1.7 eV, respectively. It is interesting to note that for occupied states this expected behavior of exact correlation of the KS theory is similar to the role of correlation in the many-body Green's functions approach. There, the many-body correlation shift the eigenvalues, or rather the poles of the one-particle Green's functions, in the opposite direction as the Hartree-Fock shift. The well-known effect is that binding energies of occupied states are much too strong within Hartree-Fock. It turns out that the EXX-KS occupied states are also more bound than the expected exact KS states, but the effect is much smaller than in the Hartree-Fock theory. The analogy breaks down for empty states. In this case, EXX results in still deeper unoccupied states than in experiment and adding LDA correlation makes them even deeper. On the other hand, Hartree-Fock theory hardly binds at all. This striking difference between the EXX and Hartree-Fock theories is because Hartree-Fock only has an asymptotic $-1/r$ potential for the occupied states and has an exponentially decaying potential for the empty states. In contrast, the KS V_{XC} potential has a Coulombic tail for all states. One says, that the Hartree-Fock potential is self-interaction free only for occupied states, whereas the KS potential (exact and EXX) is self-interaction free for all states.

For the heavier atoms Kr and Xe, we perform a full relativistic OEP calculation as relativistic effects should be important. In these cases, we do not have exact KS potentials or eigenvalues with which to compare the results. However, a comparison with the experimental first ionization potential shows that, when the spin-orbit interaction is neglected, the exact-exchange calculation gives a slightly overbound uppermost occupied level. Here again, LDA correlation lower the eigenvalues too far. It is clear that for all noble-gas atoms adding LDA correlation to exact KS exchange deteriorates the one-electron properties. The same is true when the correlation is given by the generalized-gradient approximation (GGA), however, in this case the differences between the approximate and exact KS eigenvalues are smaller.[21]

So far we have compared LDA, EXX, and EXXc-KS eigenvalues with the exact ones, where available, and with the experimental first ionization potential and binding energies of unoccupied states. For finite systems, it is possible to relate certain excitations with total-energy differences. This is the case for the first ionization potential $I=E[N-1]-E[N]$, electron affinity $A=E[N]-E[N+1]$, and the energy gap E_g, Eq. (1). The electron affinity A as defined by a total-energy difference is zero within LDA theory for most atoms. This is because in LDA the corresponding $N+1$ electron system is not bound. In the case of noble-gas atoms, however, the experimental affinity does vanish, and the LDA result is fortuitously correct. Since the affinity vanishes, the gap must equal the ionization energy. The same argument is valid for EXX. On the other hand, EXXc gives a small but finite value for the affinity. Table III shows the atomic energy gaps E_g, both experimental and calculated from total-energy differences within LDA, EXX, and EXXc. These energy gaps are compared to the KS eigenvalue differences $\epsilon_{N+1}(N)-\epsilon_N(N)$. In addition, the (triplet-singlet averaged) first optical gap is presented $\overline{\Delta}_{opt}$, as well as calculated in each method *total-energy optical gap* $\Delta^*=E[N]^*-E[N]$. Here. $E[N]$ is the total ground-state energy and $E[N]^*$ is the self-consistent total energy of an excited state in which there is a hole in the uppermost p shell and an electron in the next s shell.

TABLE III. Fundamental energy gaps $E_g=I$-A and optical gaps from experiment and calculations in neutral atoms Ne, Ar, Kr, and Xe. $\overline{\Delta}_{opt}$ is the multiplet-averaged experimental transition energy from the ground state to p^5s^1 state. Δ^* is the calculated total-energy difference between the excited atom in the (p^5s^1) configuration and the ground state. $\Delta\epsilon_{Kohn-Sham}$ is the Kohn-Sham gap.

		Ne	Ar	Kr	Xe
Expt	E_g	21.56	15.76	14.00	12.13
Expt	$\overline{\Delta}_{opt}$	16.63	11.57	9.94	8.35
LDA:	E_g	22.66	16.17	14.44	12.73
	Δ^*	17.74	11.96	10.32	8.87
	$\Delta\epsilon_{Kohn\text{-}Sham}$	13.47	10.14	8.76	7.50
EXX:	E_g	19.83	14.77	13.22	11.66
	Δ^*	15.16	10.96	9.58	8.32
	$\Delta\epsilon_{Kohn\text{-}Sham}$	17.91	11.70	9.81	8.12
EXXc:	E_g	21.31	16.03	14.61	12.79
	Δ^*	16.08	11.72	10.28	8.97
	$\Delta\epsilon_{Kohn\text{-}Sham}$	18.99	12.54	10.58	8.82

First, we note that the KS gap rather poorly approximates the experimental fundamental gap. The average deviation over the four elements between the KS and true gaps is 5.9, 4.0, and 3.1 eV for LDA, EXX, and EXXc, respectively. As shown by the data, LDA KS gaps deviate the most. When expressed in percents, LDA, EXX, and EXXc-KS gaps account for 63%, 75%, and 80% of the experimental fundamental atomic gaps, respectively. For Ne (Table I), the highly accurate KS energy gap amounts to 77% of the experimental one. For Ar (Table II) we could only estimate the exact KS gap to be of about 68% of the experimental one. The situation changes when we compare KS gaps to experimental optical gaps. It turns out that LDA, EXX, and EXXc reproduce the atomic optical gaps with 13%, 3%, and 9% accuracy, respectively. The highly accurate KS gap of Ne amounts to 99.9% of the optical gap. In particular, the good agreement of the EXX method with experiment is to be noted. An interesting question is whether similar trends take place in the solid phase. We might expect the answer to be yes if the solid is composed of a bunch of weakly interacting atoms.

When we compare the experimental fundamental gap of noble-gas atoms with the calculated total-energy differences [Eq. (1)] the agreement is fairly good. Across four elements, LDA, EXX, and EXXc reproduce the experimental atomic gaps on average to 4%, 6%, and 3% accuracy, respectively. Performing a similar although less rigorously justified total-energy calculation of *optical gaps* the agreement amounts to

TABLE IV. Equilibrium cubic lattice spacing (in a.u.) from experiment and calculations. Percents show the diviations of the lattice constant from experiment.

	Ne	Ar	Kr	Xe
a^{Expt}	8.44	9.94	10.66	11.59
a^{LDA}	7.29	9.35	10.13	11.14
	13.6%	5.9%	5.0%	3.9%
a^{EXX}	7.23	10.13	11.07	12.66
	14.3%	1.9%	3.8%	9.2%
a^{EXXc}	7.06	9.80	10.77	12.06
	16.4%	1.4%	1.0%	4.1%

5%, 5%, and 4% for LDA, EXX, and EXXc, respectively. What is remarkable is that for a total-energy difference calculations accounting for correlation seems to be very important. In fact, the best total-energy difference results come from the EXXc method, the worse with the pure EXX one.

In the following section we will investigate whether similar trends take place in the solid phase.

III. NOBLE-GAS SOLIDS: Ne, Ar, Kr, AND Xe

We performed our calculations for noble-gas solids within the pseudopotential and plane-wave formalism. For each approximate E_{xc} (LDA, EXX, and EXXc), a pseudopotential was generated using the same functional.[22] We followed the EXX plane-wave formalism developed by Görling[12] and Städele *et al.*[13] This formalism had been applied in our previous publication.[15] The plane-wave cutoff ranged between 50 and 120 Ry depending on the material and whether the structural or electronic properties were investigated. For solid krypton and xenon, the spin-orbit interaction was taken into account perturbatively.

In Table IV the experimental and calculated equilibrium fcc lattice constants are presented. The percent deviations from experiment are also given. As already noted, noble-gas solids resemble loosely bound isolated atoms. For such systems the total energy only weakly depends on the interatomic distance. The energy-volume curve is very flat and the system hardly binds. In the absence of stronger interatomic interactions, a theoretical determination of equilibrium properties is subject to a rather large uncertainty. Usual convergence criteria for total-energy determination can easily become insufficient and minor computational details, e.g., details of the pseudopotential construction can matter. For all these reasons we have checked our LDA results against independent results from publicly available LDA codes.[23,24]

As shown in Table IV, the structural equilibrium properties of noble-gas solids are very poorly described by all the methods. For example, the error in the estimate of the lattice constant for neon is more than 13%. This discrepancy is unusually large; for most solids, the LDA gives a lattice-constant estimate within about 1–2 %. For Ar, Kr, and Xe, the LDA discrepancy is on the order of 5%. Although not as dramatic as for Ne, this disagreement is still much larger than usual. Using the EXX method without correlation does not help much; the disagreement with experiment is just as large as in the other two cases. In contrast to LDA which underestimates the lattice spacing, the EXX method overestimates it for Ar, Kr, and Xe. With the exception of neon, the combined method, exact-exchange plus LDA correlation (EXXc), is the closest to experiment, but it is still not perfect. This result is similar to what was seen in the previous section's atomic calculations. For total-energy differences, the EXXc method gives the most accurate results. It is worth noting, that none of these approximations properly account for the long-range van der Waals interactions that are responsible for the binding of noble-gas solids. It is not surprising that structural properties differ so much from experiment.

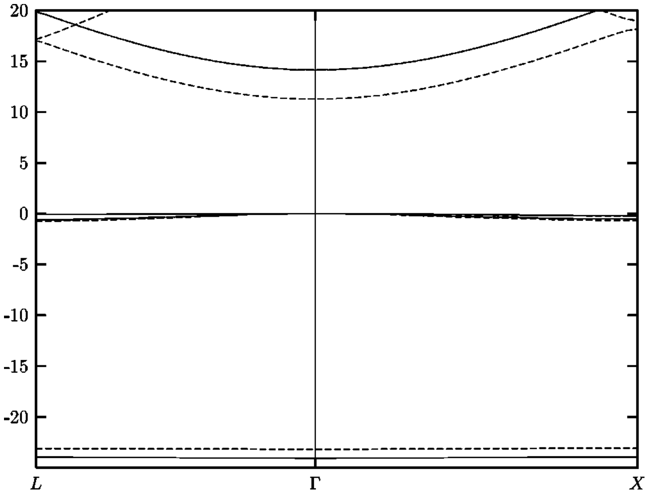

FIG. 1. Band structure of Ne along L-Γ-X directions calculated within EXX (solid lines) and LDA (dashed lines).

Figures 1–4 show the band structures along the L-Γ-X directions for Ne, Ar, Kr, and Xe with Kr and Xe being treated relativistically. The solid lines represent the EXX band structure, the dashed lines correspond to the LDA one. In Table V the KS energy gaps are compared with the experimental absolute energy gaps and with the corresponding optical gaps for solid Ne, Ar, Kr, and Xe. It is important to keep in mind that for this special class of elements, the de-

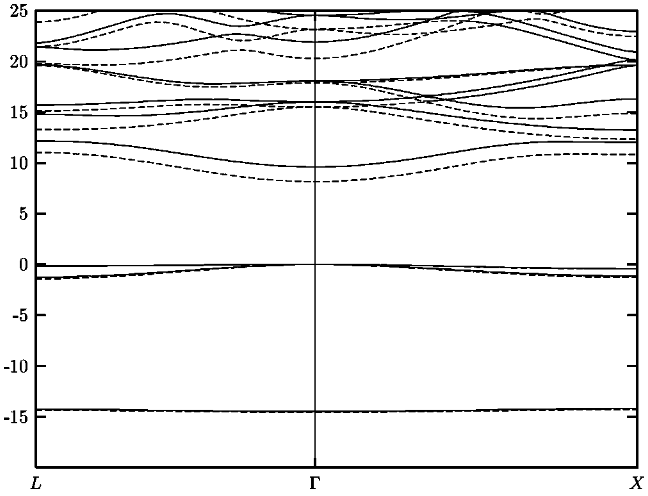

FIG. 2. Band structure of Ar along L-Γ-X directions calculated within EXX (solid lines) and LDA (dashed lines).

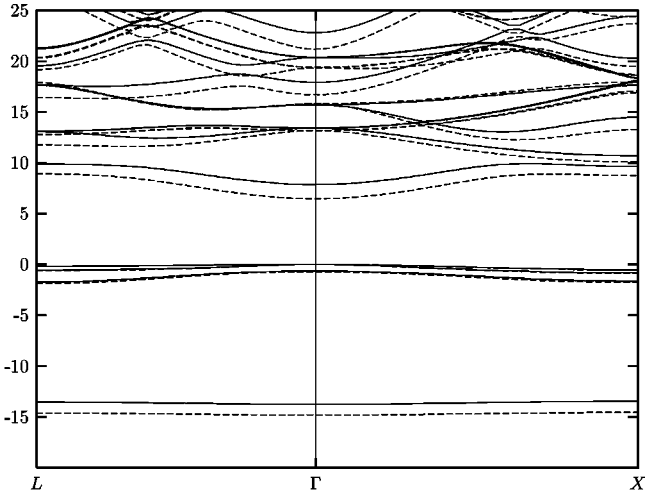

FIG. 3. Band structure of Kr along L-Γ-X directions calculated within EXX (solid lines) and LDA (dashed lines). Spin-orbit splitting included.

scription of the electronic structure provided by LDA, EXX, and EXXc might be expected to work less accurately in the solid phase than for isolated atoms. This is because in addition to only approximating short-range correlation, our functionals do not account for the long-range van der Waals effects.

Nevertheless, it is interesting to consider how well LDA, EXX, and EXXc describe the electronic structure of noble-gas solids. In LDA, the KS gaps are on average 55% of the experimental gaps. This is a typical result for solids, and though slightly less accurate than for the atomic limit given by LDA. For noble-gas solids EXX and EXXc reproduce about 68% of the fundamental gap, whereas in the atomic limit the KS gap ranged on average to 74% and 79% of the experimental fundamental gap for EXX and EXXc, respectively. The fact that the EXX and EXXc KS gaps in noble-gas solids are not very close to the experimental fundamental gaps is a central result of our investigation. The atomic results suggested that the EXX-KS gaps should be close to the optical gaps. Since the noble-gas solids have a large exciton binding energy, the optical gap is appreciably smaller than the fundamental gap. What we observe in Table V is that the EXX and EXXc KS gaps are still significantly smaller than optical gaps in noble-gas solids. They amount to about 80–81% of the experimental optical gaps, whereas the agreement is 97% in the atomic limit.

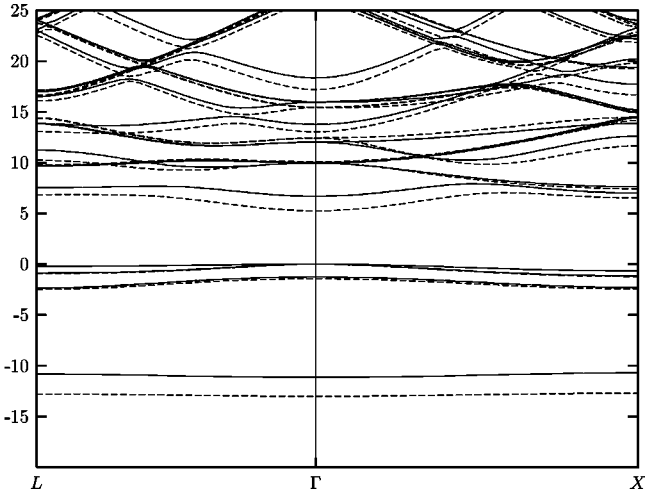

FIG. 4. Band structure of Xe along L-Γ-X directions calculated within EXX (solid lines) and LDA (dashed lines). Spin-orbit splitting included.

TABLE V. Calculated and measured energy gaps in noble-gas solids are in eV. E_g^{LDA}, E_g^{EXX}, and E_g^{EXXc} are Kohn-Sham gaps from LDA, pure EXX, and EXX plus LDA correlation, respectively. E_g^{Expt} is the experimental fundamental gap. Δ is the experimental optical gap.

	E_g^{LDA} (eV)	E_g^{EXX} (eV)	E_g^{EXXc} (eV)	E_g^{Expt} (eV)	Δ^{Expt} (eV)
Ne	11.32	14.15	14.76	21.4	17.4
Ar	8.16	9.61	9.95	14.2	12.2
Kr	6.47	7.87	8.02	11.6	10.2
Xe	5.26	6.69	6.51	9.8	8.4

The valence bands show very little dispersion in Figs. 1–4. Furthermore, the energy distance between occupied *s* and *p* bands is very close to the KS energy gap between *s* and *p* valence states in the isolated atoms. This confirms the popular picture that rare-gas solids are composed of almost undisturbed atoms. However, the conduction bands exhibit a rather pronounced dispersion. It would be interesting to verify this result experimentally. Clearly, an indirect confirmation is the fact that the experimental optical gap of the solid is always larger than the optical gap in the corresponding atom: The hole and the electron attract each other strongly if they are both localized on the same atom. In the solid, on the other hand, the hole is similarly localized as in the atom, while the electron in the conduction band is more delocalized, leading to a weaker interaction with the hole.

Another remarkable result is that the total valence-band width resulting from LDA is smaller than the one from EXX for neon. For argon, both widths are comparable. For krypton and xenon, the EXX width is smaller. We recall that previous EXX calculations have shown that for *sp* semiconductors, EXX leads to narrower total valence-band widths than in LDA. Only for diamond was the opposite observed.

IV. CONCLUSIONS

We have applied the exact-exchange method within density-functional theory to the noble-gas solids, Ne, Ar, Kr, and Xe. It was previously shown for He, Be, and Ne atoms that the Kohn-Sham energy gap coming from a nearly exact KS potential is an excellent approximation to the atomic optical gap but not to the fundamental (quasiparticle) gap. The EXX-KS gaps for these atoms are also in very good agreement (3% in average) with experimental optical gaps. A central question of our investigation was whether the same holds for the noble-gas solids. It turns out that, in contrast to previous results for *sp* semiconductors, the EXX-KS gaps in noble-gas solids are appreciably smaller than the experimental fundamental gaps. Moreover, they are also smaller by 20% than the experimental optical gaps. The results of our investigation clearly show that the EXX method does not provide a KS band structure that agrees equally well with experiment for semiconductors and insulators.

ACKNOWLEDGMENTS

We would like to thank J. A. Majewski and M. Moukara for making available their EXX-pseudopotential-generation code[22] and U. von Barth for valuable discussions. We thank X. Gonze for making available the *nearly exact* KS potential of the Ne atom. Financial support from the Deutsche Forschungsgemeinschaft (Grant No. SFB 410) is acknowledged (A. Fleszar). R. Magyar was funded by a grant from the German Academic Exchange Service (DAAD) and under NSF grant, Grant No. CHE-9875091. Some calculations were performed at the Forschungszentrum Jülich, part at the HLRS Stuttgart.

---

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

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

[3] R. M. Dreizler and E. K. U. Gross, *Density-Functional Theory, An Approach to the Quantum Many-Body Problem* (Springer, Berlin, 1990).

[4] E. Runge and E.K.U. Gross, Phys. Rev. Lett. **52**, 997 (1984).

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

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

[7] J.D. Talman and W.F. Shadwick, Phys. Rev. A **14**, 36 (1976).

[8] T. Grabo, T. Kreibich, S. Kurth, and E.K.U. Gross, in *Strong Coulomb Correlation in Electronic Structure: Beyond the Local Density Approximation*, edited by V. I. Anisimov (Gordon and Breach, Tokyo, 2000).

[9] T. Kotani, Phys. Rev. B **50**, 14 816 (1994).

[10] T. Kotani, Phys. Rev. Lett. **74**, 2989 (1995).

[11] T. Kotani and H. Akai, Phys. Rev. B **54**, 16 502 (1996).

[12] A. Görling, Phys. Rev. B **53**, 7024 (1996); **59**, 10 370(E) (1999).

[13] M. Städele, J.A. Majewski, P. Vogl, and A. Görling, Phys. Rev. Lett. **79**, 2089 (1997); M. Städele, M. Moukara, J.A. Majewski, P. Vogl, and A. Görling, Phys. Rev. B **59**, 10 031 (1999).

[14] W.G. Aulbur, M. Städele, and A. Görling, Phys. Rev. B **62**, 7121 (2000).

[15] A. Fleszar, Phys. Rev. B **64**, 245204 (2001).

[16] A. Savin, C.J. Umrigar, and X. Gonze, Chem. Phys. Lett. **288**, 391 (1998).

[17] A.I. Al-Sharif, R. Resta, and C.J. Umrigar, Phys. Rev. A **57**, 2466 (1998).

[18] C. J. Umrigar and X. Gonze, in *Proceedings of the Mardi Gras '93 Conference*, edited by D.A. Browne *et al.* (World Scientific, Singapore, 1993).

[19] Q. Zhao, R.C. Morrison, and R.G. Parr, Phys. Rev. A **50**, 2138 (1994).

[20] R.C. Morrison and Q. Zhao, Phys. Rev. A **51**, 1980 (1995).

[21] We have done a series of atomic calculations using the GGA correlation functional from J.P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996); **78**, 1396(E) (1997).

[22] M. Moukara, M. Städele, J.A. Majewski, P. Vogl, and A. Görling, J. Phys.: Condens. Matter **12**, 6783 (2000).

[23] The ABINIT code, a common project of the Université Catholique de Louvain, Corning Incorporated, and other contributors (URL http://www.abinit.org).

[24] The FHI98MD code of the Fritz-Haber-Institut, Berlin (URL http://www.fhi-berlin.mpg. de/th/fhimd/).