

Exact Kohn-Sham direct gap at an insulator-metal transition

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The alternate molecular orbital ground state for the cubic electron gas (three-dimensional analogue of the two-plane-wave model) has an insulator-metal transition at $r_s \simeq 100$. In contrast, the eigenvalues of the exact Kohn-Sham potential are metallic at all r_s .

I. INTRODUCTION

It is well known that the one-electron eigenvalues generated by local-spin-density approximations (LSDA) to density-functional theory (DFT) do not predict the fundamental gap ϵ_g for semiconductors and insulators correctly.¹ The essential source of the discrepancy is not the LSDA, but neglect of a discontinuity Δ (in N , the total electrons) in the functional derivative $\partial E_{xc}/\partial n$ which generates the exchange-correlation part of any Kohn-Sham (KS) potential, either exact or LSDA.²

Nearly ubiquitous use of KS eigenvalues (in spite of their deficiencies) as valid spectroscopic energies makes it important to study reasonably realistic systems that are simple enough that the exact KS potentials V_{xc} , their eigenvalues, the exact excitation energies, and hence Δ , all can be determined. Light atoms are one obvious choice, since the electron excitation energies from a high-quality correlated wave function can be compared to the eigenvalues of the potential which generates the same density as that determined by the wave function. Several light-atom studies³⁻⁵ have shown that such KS eigenvalues do not correspond well with the true excitation energies. Since the one electron spectra of light atoms have a nonvanishing gap, those studies could not consider the dependence of Δ on gap size nor, of course, any extended system effects.

Such effects have been considered in a recent calculation for crystalline Si.⁶ The exact KS eigenvalues differ remarkably little from the LSDA eigenvalues, while DFT-based one-electron propagator energies are quite close to experiment. The latter result was found earlier^{7,8} to be broadly true for various other semiconductors as well. However, none of these studies considered the dependence of Δ on the size of the KS gap. The importance of an extended three-dimensional system for which Δ can be determined directly as a function of KS gap size is illustrated particularly well by crystalline Ge, which has zero gap in LSDA.^{8,9}

The two-plane-wave model^{2(c)} (TPWM) is a quasi-one-dimensional version of a system which has been used to study the gap-size dependence of Δ .^{10,11} It models the semiconductor as a linear chain with the electronic basis functions localized to within $1/B_p$ in the y - z plane by a

factor $\zeta(y,z)$ and restricted to a pair of plane waves along x

$$\phi_{\pm k} = L^{-1/2} \exp[i(k \pm B)x] \zeta(y,z), \quad (1)$$

with $2B = Q$ equal to the Brillouin-zone (BZ) length. In previous work, Δ was calculated in the TPWM in exchange-only DFT (XODFT; see below) at first order in perturbation theory (cf. Sec. IV, Ref. 12) and at the random-phase approximation (RPA) level of exchange correlation¹¹ (without self-consistent iteration of the self-energy, screened-interaction, dielectric-function, Green's-function loop).

Here we connect the TPWM with a long-known three-dimensional model system whose properties are both easy to grasp and amenable to direct calculation purely within a wave-function treatment. We show, without analytical approximation, that the KS eigenvalues fail (completely) to describe the evolution of the one-electron behavior with system density.

II. THE ALTERNANT-MOLECULAR-ORBITAL (AMO) ELECTRON GAS

The alternant-molecular-orbital (AMO) state¹³ is a particular generalized Hartree-Fock state that enables inclusion of electron correlation via an axial spin-density wave.^{14,15} An extensive study of the electron gas in the AMO state has been described elsewhere.^{16,17} Two critical results are (1) the exact one-electron energies are known (at the level of Koopmans' theorem) since the AMO is a single-determinantal state, and (2) there is a metal-insulator transition¹⁸ at $r_s \simeq 100$ as the system is driven towards the Wigner lattice limit.

To make connection with the TPWM and provide the basis for our results, we summarize pertinent features of the AMO state. The restricted Hartree-Fock (RHF) one-body states for the electron gas are simple plane waves $\eta(\mathbf{k},\mathbf{r})$ doubly occupied within a spherical Fermi volume. For the AMO electron gas, the RHF occupation is modified so that all $\eta(\mathbf{k},\mathbf{r})$ within a cubic¹⁹ Fermi volume are doubly occupied. The AMO state is a single determinant of one-electron states $\psi_{k,s}$ in which each RHF-occupied η is allowed to mix with one RHF virtual η according to

$$\psi_{\mathbf{k},1} = u(\mathbf{k})\eta(\mathbf{k},\mathbf{r}) + v(\mathbf{k})\eta(\bar{\mathbf{k}},\mathbf{r}) \quad (\text{spin up}), \quad (2)$$

$$\psi_{\mathbf{k},2} = u(\mathbf{k})\eta(\mathbf{k},\mathbf{r}) - v(\mathbf{k})\eta(\bar{\mathbf{k}},\mathbf{r}) \quad (\text{spin down}), \quad (3)$$

with $u(\mathbf{k})$ and $v(\mathbf{k})$ variational parameters subject to the normalization condition

$$u^2(\mathbf{k}) + v^2(\mathbf{k}) = 1 \quad (4)$$

The vector $\bar{\mathbf{k}}$ is chosen by adding that simple-cubic reciprocal-lattice vector K_0 that takes \mathbf{k} into the second Brillouin zone (bcc direct lattice symmetry having been imposed). At any given r_s the optimal AMO state defines an exact model system state.

Enforcing cubic symmetry on the RHF Fermi surface of course increases the energy of the system relative to spherical RHF, but the AMO mixing of the η 's then lowers it. For $r_s > 25$, the decrease in the potential energy due to mixing predominates, and the AMO is energetically favored over the spherical RHF state. This result is intuitively accessible by noting that the AMO state generates a cosine-modulated spin density

$$n_{\pm}(\mathbf{r}) = (N/2V) \{ 1 \pm (\lambda/3) [\cos(K_0x) + \cos(K_0y) + \cos(K_0z)] \} \quad (5)$$

with $+$ ($-$) for spin up (down) and λ determined from the $v(\mathbf{k})$. The AMO state gets its name from this spin correlation. The total electron density is uniform: $n(\mathbf{r}) \equiv N/V = n$, so there is no electrostatic penalty to pay for the separation of the charges. The amplitude of the cosine modulation λ is plotted as a function of r_s in Fig. 1.

Since the AMO wave function is a single-determinant state, its single-particle energies are determined once the minimizing form of $v(\mathbf{k})$ is known. Those energies at two densities are shown in Fig. 2. For larger densities there is indirect band overlap and the system is a conductor. At lower densities it is a semiconductor; see Fig. 3 for ϵ_g as a function of r_s . (The band gap is small compared to real systems because it is provided strictly by spin correlation.)

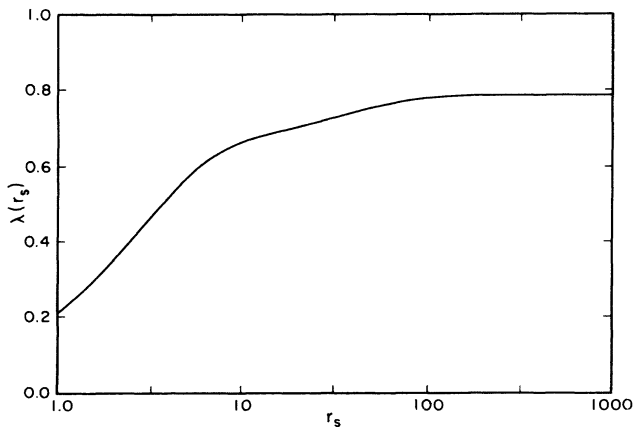


FIG. 1. Amplitude of cosine modulation λ of the spin density as function of r_s .

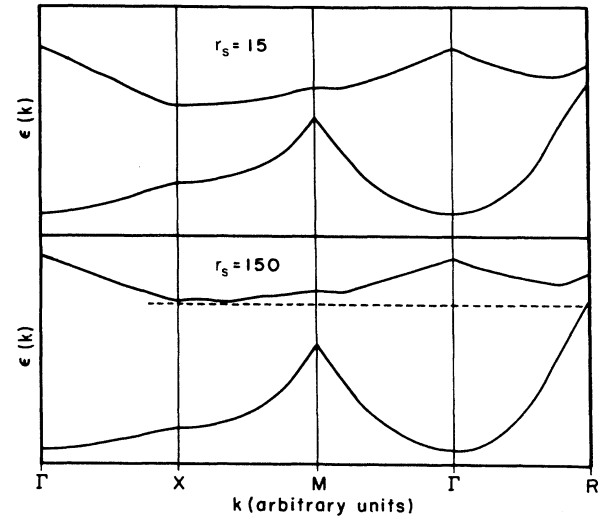


FIG. 2. AMO cubic electron gas single-particle energies for $r_s = 15$ and 150.

III. DENSITY-FUNCTIONAL THEORY OF THE AMO ELECTRON GAS

Because the AMO is a generalized Hartree-Fock state, the distinction²⁰ between Hartree-Fock DFT (HFDFT) and exchange-only DFT (XODFT) is relevant. In HFDFT the total energy is the actual restricted Hartree-Fock value, while the local KS potential is that which reproduces the RHF electron density. In general the HFDFT and RHF orbitals are not identical. XODFT in contrast generates the total energy and electron density from a single determinant with doubly occupied orbitals restricted to those which can be generated from a local potential. On variational grounds $E_{\text{XODFT}} \geq E_{\text{HF}}$.

With the full AMO cubic electron gas solution available, it is straightforward to determine the associated HFDFT results by finding the effective one-body potentials that generate the AMO spin density (since the Hohenberg-Kohn theorem²¹ is a uniqueness theorem).

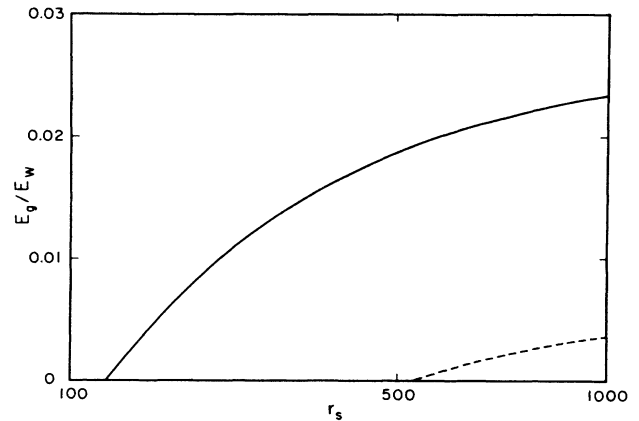


FIG. 3. Solid curve: energy gap of the AMO cubic electron gas as a function of r_s (normalized by the valence-band width for given r_s). Dashed curve: normalized XODFT energy gap.

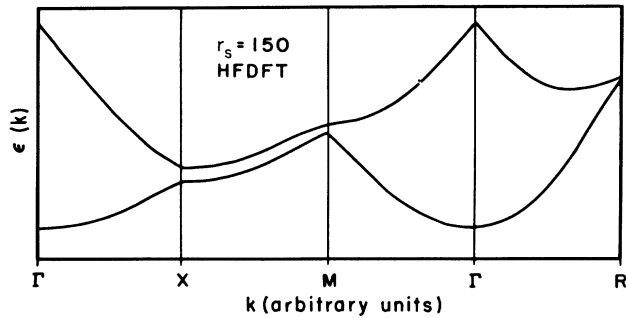
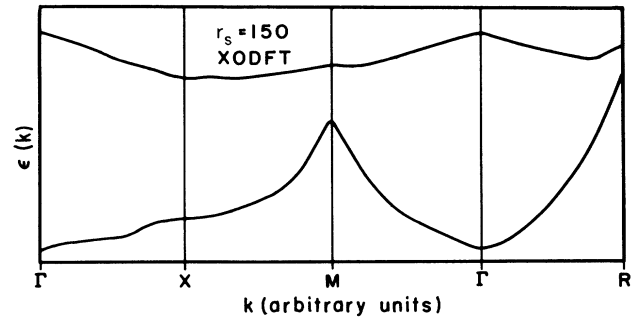
FIG. 4. Kohn-Sham eigenvalues for HFDFT at $r_s = 150$.

FIG. 5. As in Fig. 4 for XODFT.

The Hamiltonian will contain two local potentials, one for each spin. Since the spin density is a simple cosine modulation, it is sufficient to expand both the potential and the wave functions in a plane-wave basis, then solve (numerically) for the potential coefficients that generate the required density.

The HFDFT eigenvalue spectra which those KS potentials generate is shown for $r_s = 150$ in Fig. 4. The surprising result is that HFDFT always makes the system metallic; there is no gap in the HFDFT-KS eigenvalue spectrum for any value of the density obtained in the AMO calculation. Thus, the exact DFT fails to give even the qualitatively correct result for this system. Since there must be a gap for $r_s \geq 100$, its magnitude is the value of Δ .

XODFT for the cubic electron gas is generated by redoing the AMO calculation with the additional constraint that only AMO determinants populated with states from an independent-particle Hamiltonian be admitted. That is, the allowed values of $v(\mathbf{k})$ are restricted to those obtainable from a KS potential. The procedure is a three-dimensional, variational version of the TPWM calculation of Ref. 10. Assuming a weak, symmetry-restricted (in the sense of omission of higher Fourier coefficients) KS potential, it must be of the form

$$V(\mathbf{r}) = V[\cos(K_0x) + \cos(K_0y) + \cos(K_0z)]. \quad (6)$$

With orbitals of AMO form [Eqs. (2) and (3)] and variational determination of the constrained parameters $v_X(k)$ and $u_X(k)$ (subscripted to distinguish XODFT from general AMO), one finds

$$u_X(\mathbf{k}) = \cos\theta_k, \quad v_X(\mathbf{k}) = \sin\theta_k, \quad (7)$$

$$\tan(2\theta_k) = V/(k_i K_0), \quad (8)$$

where k_i is the largest magnitude component of \mathbf{k} . Thus, while the general AMO calculation is free to choose any values of the $v(k)$ parameters, XODFT restricts consideration to a specific one-parameter family. The resulting XODFT one-electron spectrum for $r_s = 150$ is shown in Fig. 5. There is no gap. XODFT does eventually generate a gap, at $r_s > 500$. Comparison with the exact AMO gap (Fig. 3) makes explicit an important result. Imposition of the AMO form (i.e., physically correct form for this model) on the KS orbitals does result in a KS spectrum with qualitatively correct behavior (a metal-insulator transition) but the quantitative behavior is grossly in error.

This result is a clear caution regarding interpretation of KS spectra generated with the nearly universal practice, for real systems, of constraining the KS orbitals to physically realistic symmetries (that is, irreducible representations of the appropriate symmetry group). The present calculation suggests strongly that the outcome may be qualitatively plausible yet quantitatively meaningless. These results are also an unambiguous counterexample to the commonplace assumption that HFDFT and XODFT are virtually interchangeable.

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