

Many-body effects on the electron states of solid argon

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(Received 28 September 1983)

We consider many-body effects on the band structure of solid argon within the Coulomb-hole-plus-screened-exchange approximation, and with the use of a basis set of orthogonalized plane waves. The difficulties inherent to the nonlocal character of the self-energy operator are overcome by expressing the crystal density matrix in terms of localized Gaussian functions. A major advantage of this technique is that all the matrix elements necessary to perform the correlated band-structure calculation can be computed analytically. Our results for the case of argon are compared with experiments and with previous theoretical works.

I. INTRODUCTION

In recent years considerable effort has been devoted toward efficient solutions of the Hartree-Fock (HF) equations in solids.^{1,2} The orthogonalized-plane-wave method (OPW) has proved to be a valuable tool for HF calculations,^{3,4} and recent improvements have further clarified the advantages of this versatile tool.⁵ Other methods which have been fruitfully adopted for first-principles band-structure calculations are the local-orbital and the mixed-basis methods.^{2,6}

The HF calculations are a necessary, though preliminary, step before considering many-body effects. In order to limit computational difficulties, correlation effects have been often treated in the literature according to specific *ad hoc* models.⁷ This occurred in spite of the fact that powerful approaches based on Green's-function techniques have opened a major conceptual breakthrough in the field of electronic state calculations.^{8,9} The simplest many-body approach to include *ab initio* correlation effects in band-structure calculations is the one first proposed by Hedin⁸ and known as the Coulomb-hole-plus-screened-exchange approximation (COHSEX). Within this theoretical framework, we find the pioneering works of Brinkman and Goodman³ on Si, of Lipari and Fowler⁴ on Ar, and the perturbative approach of Brener⁹ on LiF.

In this paper we extend an efficient technique,⁵ previously proposed to treat exactly the integro-differential HF equations in crystals, to the case where correlation effects are included within the COHSEX approximation. Using a basis set of OPW's and expressing the density matrix of the crystal in terms of localized Gaussian-type orbitals (GTO's) [we refer to this procedure as the Gaussian orthogonalized-plane-wave method (GOPW)], we are able to express analytically all the necessary matrix elements. This leads to a drastic reduction in computational labor and to a much increased numerical accuracy. As a specif-

ic example, we consider the case of argon, for which we compare our results with experimental data and with other theoretical works.

II. GAUSSIAN OPW METHOD FOR THE COHSEX SECULAR EQUATION

A. Introductory remarks

The GOPW method^{5,11} has been successfully applied to the solution of the HF equations for a crystal as has been described elsewhere.⁵ The simplicity of the method is related to the combined use of GTO's for describing the density matrix of the crystal and of OPW's for describing valence and/or conduction states, and it has had success in describing both the localized and the itinerant nature of the electron states. The purpose of this paper is to apply it to the solution of the integro-differential COHSEX equations.

The single-particle-like excitations of a closed-shell many-electron system are described by the effective-wave equation:

$$[h(\vec{r}) + V(\vec{r})]\phi(\vec{r}) + \int \Sigma(\vec{r}, \vec{r}'; E)\phi(\vec{r}')d\vec{r}' = E\phi(\vec{r}),$$

$$h(\vec{r}) = -\frac{\hbar^2}{2m}\nabla^2 - \sum_{\vec{R}_n} \frac{Z_n e^2}{|\vec{r} - \vec{R}_n|}, \quad (1)$$

$$V(\vec{r}) = e^2 \int \frac{\rho(\vec{r}', \vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}',$$

where $h(\vec{r})$ is the one-electron Hamiltonian, $V(\vec{r})$ is the Hartree potential, $\Sigma(\vec{r}, \vec{r}'; E)$ is the non-local energy-dependent self-energy operator,⁸ and $\rho(\vec{r}, \vec{r}')$ is the spin-independent one-electron density matrix of the system.

We consider the self-energy operator in the COHSEX approximation and also assume that local-field effects^{12,13}

in the dielectric screening can be neglected, i.e., the nondiagonal elements of the dielectric matrix can be disregarded. With these assumptions, one obtains

$$\Sigma(\vec{r}, \vec{r}'; E) \simeq -\frac{1}{2}\rho(\vec{r}, \vec{r}')W(\vec{r}-\vec{r}') + E_{Ch}\delta(\vec{r}-\vec{r}'), \quad (2)$$

where $W(\vec{r}-\vec{r}')$ is the statically screened Coulomb interaction and the Coulomb-hole term E_{Ch} is

$$E_{Ch} = \frac{1}{2} \int \frac{d\vec{q}}{(2\pi)^3} \frac{4\pi e^2}{q^2} \left[\frac{1}{\epsilon(q)} - 1 \right], \quad (3)$$

B. Analytic expression of the screened exchange bielectronic integrals

We consider first the case of two plane waves and two 1s GTO's, since the general case of occupied states of arbitrary angular momentum can be easily treated by differentiation techniques:

$$J_s(\vec{k}_i, \alpha; \lambda; \beta, \vec{k}_j) \equiv \int d\vec{r}_1 d\vec{r}_2 e^{-i\vec{k}_i \cdot \vec{r}_1} Y_{00}(\hat{r}_1) e^{-ar_1^2} \frac{e^{-\lambda r_{12}}}{r_{12}} Y_{00}(\hat{r}_1) e^{-Br_1^2} e^{i\vec{k}_j \cdot \vec{r}_2}, \quad r_{12} \equiv |\vec{r}_1 - \vec{r}_2|. \quad (4)$$

In order to calculate J_s , we first decouple the variables \vec{r}_1 and \vec{r}_2 by means of the standard relation:

$$\frac{e^{-\lambda r_{12}}}{r_{12}} = \frac{1}{2\pi^2} \int d\vec{q} \frac{1}{q^2 + \lambda^2} e^{i\vec{q} \cdot (\vec{r}_1 - \vec{r}_2)}. \quad (5)$$

We then take advantage of the fact that the Fourier transform of a Gaussian function is still a Gaussian function, and we obtain

$$J_s = \frac{1}{8(\alpha\beta)^{3/2}} e^{-k_i^2/4\alpha - k_j^2/4\beta} \times \int d\vec{q} \frac{1}{q^2 + \lambda^2} e^{-q^2/4\gamma + \vec{\kappa} \cdot \vec{q}}, \quad (6)$$

where the reduced exponent γ and the reduced wave vector $\vec{\kappa}$ are defined as

$$\gamma = \frac{\alpha\beta}{\alpha + \beta}, \quad \vec{\kappa} = \frac{1}{2} \left[\frac{\vec{k}_i}{\alpha} + \frac{\vec{k}_j}{\beta} \right].$$

With the representation

$$\frac{1}{q^2 + \lambda^2} = \int_0^\infty e^{-s(q^2 + \lambda^2)} ds, \quad (7)$$

$$\int e^{-a^2x^2 + b^2/x^2} dx = -\frac{\sqrt{\pi}}{4a} e^{-a^2x^2 + b^2/x^2} [w(b/x + iax) + w(-b/x + iax)] + \text{const},$$

and with some lengthy but trivial algebra, we finally arrive at the simple result

$$J_s(\vec{k}_i, \alpha; \lambda; \beta, \vec{k}_j) = \frac{\pi^2}{4\kappa(\alpha\beta)^{3/2}} \exp\left[-\frac{(\vec{k}_i - \vec{k}_j)^2}{4(\alpha + \beta)}\right] \text{Im}w\left[\kappa\sqrt{\gamma} + \frac{i\lambda}{2\sqrt{\gamma}}\right]. \quad (10)$$

In the case where one must consider p -like occupied states, one also needs integrals of the type

$$J_p(\vec{k}_i, \alpha; \lambda; \beta, \vec{k}_j) = \sum_{m=-1}^1 \int d\vec{r}_1 d\vec{r}_2 e^{-i\vec{k}_i \cdot \vec{r}_1} Y_{1m}^*(\hat{r}_1) r_{12} e^{-ar_1^2} \frac{e^{-\lambda r_{12}}}{r_{12}} Y_{1m}(\hat{r}_1) r_{12} e^{-Br_1^2} e^{i\vec{k}_j \cdot \vec{r}_2}. \quad (11)$$

They can be evaluated in terms of the J_s integrals by means of the relationship:

where $\epsilon(q)$ is the static dielectric function of the crystal.

We now discuss the handling of Eq. (1) with a kernel of type (2), within the GOPW scheme. The screened interaction $W(\vec{r}-\vec{r}')$ can be approximated to any degree of accuracy by a sum of Yukawa-type terms. We consider now the evaluation of the bielectronic exchange integrals between two plane waves and two GTO's in the case where the electron-electron interaction is of the simple Yukawa type.

Eq. (6) then becomes

$$J_s = \frac{\pi^{3/2}}{-(\alpha\beta)^{3/2}} e^{-k_i^2/4\alpha - k_j^2/4\beta} \times \int_0^\infty \frac{1}{(4s + 1/\gamma)^{3/2}} e^{\kappa^2/4s + (1/\gamma) - \lambda^2 s} ds. \quad (8)$$

Performing the change of variable,

$$\kappa^2/(4s + 1/\gamma) = t^2,$$

one obtains

$$J_s = \frac{\pi^{3/2}}{2\kappa(\alpha\beta)^{3/2}} e^{-k_i^2/4\alpha - k_j^2/4\beta + \lambda^2/4\gamma} \times \int_0^{\kappa\sqrt{\gamma}} e^{t^2 - \lambda^2\kappa^2/4t^2} dt. \quad (9)$$

It is useful to introduce at this stage the complex function $w(z)$:^{14,15}

$$w(z) = e^{-z^2} \left[1 + \frac{2i}{\sqrt{\pi}} \int_0^z e^{t^2} dt \right] \equiv e^{-z^2} \text{erfc}(-iz).$$

Using the following indefinite integral:¹⁴

$$J_p(\vec{k}_i, \alpha; \lambda; \beta; \vec{k}_j) = 3 \sum_{v=x,y,z} \frac{\partial^2}{\partial k_{iv} \partial k_{jv}} J_s(\vec{k}_i, \alpha; \lambda; \beta; \vec{k}_j). \quad (12)$$

The explicit evaluation of J_p is carried out by exploiting the recursion relations for the derivatives of the $w(z)$ function¹⁶

$$w^{(n+2)}(z) + 2zw^{(n+1)}(z) + 2(n+1)w^{(n)}(z) = 0,$$

$$w^0(z) = w(z), \quad w^{(1)}(z) = -2zw(z) + \frac{2i}{\sqrt{\pi}}.$$

The final result is

$$J_p(\vec{k}_i, \alpha; \lambda; \beta; \vec{k}_j) = \frac{3\pi^2}{16\kappa(\alpha\beta)^{5/2}} \exp\left[-\frac{(\vec{k}_i - \vec{k}_j)^2}{4(\alpha + \beta)}\right] \\ \times \left\{ \left[\frac{\vec{\kappa} \cdot (\vec{k}_i + \vec{k}_j)}{\kappa^2} + \vec{k}_i \cdot \vec{k}_j - \lambda^2 \right] \text{Im} w \left[\kappa\sqrt{\gamma} + \frac{i\lambda}{2\sqrt{\gamma}} \right] \right. \\ \left. + \frac{\vec{\kappa} \cdot (\vec{k}_i + \vec{k}_j)}{\kappa} \left[\lambda \text{Re} w \left[\kappa\sqrt{\gamma} + \frac{i\lambda}{2\sqrt{\gamma}} \right] - 2 \left[\frac{\nu}{\pi} \right]^{1/2} \cos(\lambda\kappa) \right] + \frac{4}{\sqrt{\pi}} \kappa\gamma^{3/2} \right\}. \quad (13)$$

With the help of a standard computer routine for the function $w(z)$,¹⁶ the expressions (10) and (13) for the screened exchange integrals can be easily evaluated. The other matrix elements appearing in the GOPW method are much more simple, as already discussed elsewhere.⁵

C. Dielectric screening in solid argon

For the purposes of the present paper, it is convenient to approximate the static dielectric function of the crystal by the following interpolation formula:

$$\frac{1}{\epsilon(q)} = \frac{1}{\epsilon_s} + A_1 \frac{q^2}{q^2 + \lambda_1^2} + A_2 \frac{q^2}{q^2 + \lambda_2^2}, \quad (14)$$

where each term corresponds to an effective interaction in real space of the Yukawa type. Equation (14) automatically satisfies the requirement $\epsilon(0) = \epsilon_s = 1.67$. In order to fix the other parameters, we first observe that the high- q limiting behavior of $\epsilon(q)$ must be

$$1/\epsilon(q) \rightarrow 1 - c/q^4. \quad (15)$$

The presence in Eq. (15) of a term proportional to q^{-2} would in fact give rise to unphysical divergences in the charge response to a point-charge perturbation. We then assume that the response of the system to high- q disturbances is free-electron-like; i.e., $c = 16\pi n_0/a_B$, where n_0 is the valence electron density, and a_B is the Bohr radius. The above requirements still leave one free parameter, which is determined in such a way that the Coulomb-hole energy E_{Ch} obtained from the dielectric function (14) equals the value of 2.39 eV calculated by Lipari^{17,4} using a model first proposed by Fry.¹⁸ A value of n_0 corresponding to eight valence electrons per unit cell and to a lattice

parameter of 10.05 a.u. leads to the following values of the parameters A and λ : $A_1 = 0.4072$, $\lambda_1 = 0.4918$, $A_2 = -0.0060$, $\lambda_2 = 4.0411$.

D. Hartree-Fock and correlated energy bands of solid argon

The argon atom has the closed-shell structure $K(2)$, $L(8)$, $3s^2$, $3p^6$. The atomic data necessary for the COHSEX-OPW calculation have been computed using the same (11s/7p) GTO basis set previously adopted for the HF calculation.^{5,19} In order to obtain core-level orbital energies and wave functions which are genuine eigenvalues and eigenvectors of Eq. (1), with the self-energy operator given by Eq. (2), the atomic orbital energies and expansion coefficients have been recalculated self-consistently by screening the atomic self-energy operator with the crystal dielectric function (14) according to Eq. (2).

The crystal structure of solid argon is fcc with a lattice parameter of 10.05 a.u. In the calculation of the band structure we have used a maximum of 259 OPW's; at Γ , this corresponds to consider the first 16 shells of reciprocal-lattice vectors, up to waves of the type $\langle 442 \rangle$ and $\langle 600 \rangle$. We have considered as core levels only the genuine core shells K and L .

The COHSEX energy bands of argon are reported in Table I and displayed in Fig. 1; the symmetry notations are those of Koster *et al.*²⁰ For comparison, we have also reported the HF energy bands of Ref. 5 to which we refer for an account of other HF calculations available in the literature. A detailed account of other theoretical works on the electron states of solid argon can be found in Ref. 22.

TABLE I. Energies (eV) of crystal states in solid argon at the points Γ , X , L , and W of the Brillouin zone in the COHSEX approximation. The corresponding HF values are reported in parentheses for comparison.

Γ	X	L	W
-33.24 Γ_1^+ (-34.77)	-32.75 X_1^+ (-34.22)	-32.87 L_1^+ (-34.35)	-32.74 W_1 (-34.21)
-13.71 Γ_4^- (-14.73)	-15.29 X_2^- (-16.45)	-15.47 L_2^- (-16.58)	-14.74 W_5 (-15.72)
	-14.17 X_5^- (-15.32)	-13.75 L_3^- (-14.96)	-14.27 W_4 (-15.22)
0.91 Γ_1^+ (3.20)	3.41 X_1^+ (5.67)	4.03 L_1^+ (6.28)	4.55 W_4 (6.83)
9.58 Γ_3^+ (11.79)	5.51 X_4^+ (7.71)	6.03 L_2^- (8.28)	6.84 W_5 (9.09)
12.67 Γ_2^- (15.05)	8.11 X_2^- (10.33)	8.92 L_3^+ (11.09)	9.19 W_1 (11.48)
13.18 Γ_3^+ (15.28)	12.76 X_5^- (15.04)	12.09 L_2^- (14.45)	14.47 W_5 (16.78)
15.60 Γ_4^- (17.97)	16.31 X_3^+ (18.35)	16.04 L_3^+ (18.14)	16.85 W_1 (19.12)

In agreement with previous theoretical investigations,⁴ the correlated conduction energy bands shift almost rigidly downward of the E_{Ch} quantity with respect to the HF results. This is a consequence of the short-range character of the exchange operator and of the itinerant character of the conduction wave functions in closed-shell systems.

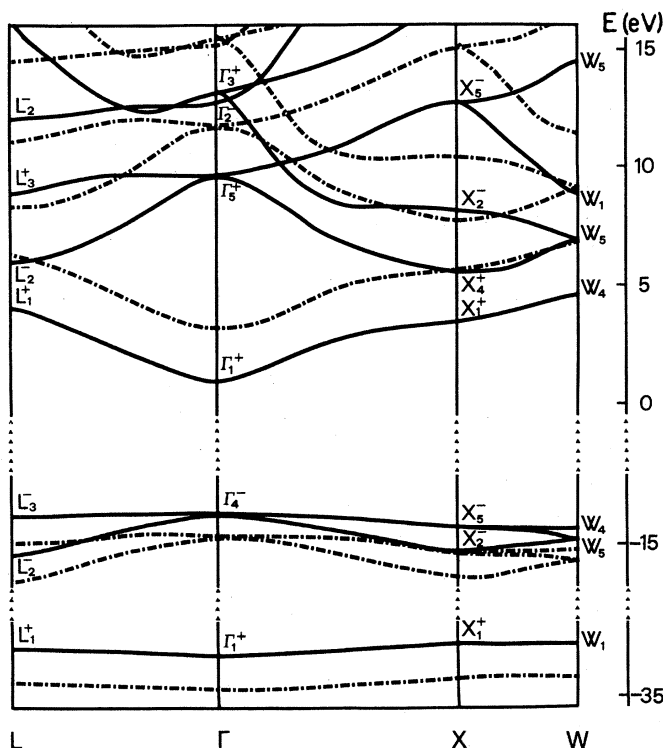


FIG. 1. Energy bands of solid argon (eV) in the COHSEX approximation (solid lines) and in the HF approximation (dashed lines).

The valence-correlated energy bands shift upward with a negligible \vec{k} dependence. This fact is essentially due to the insensitivity of the hopping integrals to screening. The $\Gamma_4^- - \Gamma_1^+$ energy gap is therefore reduced from the HF value of 17.93 eV to the COHSEX value of 14.62 eV which compares well with the experimental value of 14.15 eV.²¹ Also the electron affinity and the photoemission threshold calculated in the COHSEX approximation are in much better agreement with the experimental results²¹ than the HF values. The minimum of the conduction band decreases from 3.20 to 0.91 eV, to be compared with an experimental value of 0.4 eV. The photoemission threshold changes from 14.73 to 13.71 eV, again with substantial agreement with the estimated experimental value of 13.68 eV. The width of the 3p valence band, both in the HF and in the COHSEX approximation, is in good agreement with the observed value of 1.7 eV. We finally note that a moderate change of the Coulomb-hole energy E_{Ch} to a value of 2.90 eV would bring the values of the electron affinities and of the energy gap into perfect agreement with experiments, without affecting sensibly the photoemission threshold.

III. CONCLUSIONS

We have considered the correlation effects on the electronic states of solid argon, solving the integro-differential equation for the one-electron Green's function within the COHSEX approximation. The novelty and the accuracy of this study are essentially due to the possibility of expressing in a closed analytic form the screened exchange bielectronic integrals of interest in the COHSEX-OPW method. According to our results, one can safely state that the COHSEX approximation goes a long way indeed toward a quantitative account of many-body effects in solids, and yet it can be managed with a reasonable numerical labor.

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