Hartree-Fock energy levels in solids: Application to argon

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We examine the reliability of first-principles electronic calculations performed with the orthogonalized-plane-wave method and the Gaussian representation of occupied orbitals. A good feature of such a procedure is that the exchange potential in its nonlocal form can be included rigorously and the matrix elements are still in analytic form. As a specific application, we consider the case of argon, and we compare our results with previous calculations.

I. INTRODUCTION

The importance of first-principles band-structure calculations has focused the attention of several authors on the foundation of the methods traditionally applied in this field (see, for instance, the papers of Brener and Fry[1] and references quoted therein). In particular, the orthogonalized-plane-wave (OPW) method[2] has been thoroughly investigated in this context.[3-6] The paper of Brinkman and Goodman[3] of 1966 and that of Lipari and Fowler[4] four years later provided a numerical technique for treating rigorously the Hartree-Fock (HF) operator. In these papers[3,4] occupied atomic states are expressed in terms of Slater-type orbitals (STO); the resulting numerical technique, however, is so laborious as to prevent a routine application of the procedure. Very recently the problem has been reopened[5,6] and major simplifications have been shown to occur if occupied atomic states are expressed in terms of Gaussian-type orbitals[7] (GTO).

The main motivation of this paper is to examine the HF energy bands obtained combining the standard OPW method with the Gaussian representation of occupied orbitals; we refer to this approach as the GOPW (Gaussian OPW method). Its advantage is that all the ingredients needed for constructing the matrix elements of the secular equation (orthogonalization coefficients, Fourier transforms of the Coulomb potential, bielectronic exchange integrals) are analytic.

As a specific application we consider the case of solid argon. There is a very large number of band-structure calculations on solid argon,[4, 8-16] from the pioneering work of Knox and Bassani[8] of 1961 to the recent one of Khan and Callaway[16] of 1980; in the literature solid argon has often constituted an ideal system to test new methods and procedures. Most of these papers provide, at least in principle, the HF energy bands of argon and are thus directly comparable with our results.

In Sec. II we give the basic tools for constructing analytically the matrix elements of the GOPW method. To show its convenience, we consider in Sec. III the specific application to solid argon. Section IV contains the conclusions.

II. CONSTRUCTION OF THE MATRIX ELEMENTS OF THE GAUSSIAN OPW METHOD

A. General considerations

The OPW method has been widely used in the literature[17] mostly with the following choices: (i) occupied atomiclike states are expressed in terms of STO's, and (ii) the crystal potential is approximated as a sum of *local* atomiclike potentials. With choices (i) and (ii), the matrix elements of the OPW method can be evaluated analytically; this advantage, however, carries with it the drawback that some type of local density approximation to the exchange potential[18] has to be made.

A way to overcome this difficulty has been suggested in two previous works,[5,6] which adopt the expansion of STO's into a number, for example, N, of GTO's before computing the bielectronic exchange integrals; in those papers the value of N was set equal to four. This technique, however, becomes unnecessarily complicated when a relatively high number of STO's is put in the basis set to provide accurate HF results.[19] In this case it is convenient to abandon the mixed representation in terms of STO's and GTO's as is done in the present paper. As we shall see, all the matrix elements appearing in the GOPW method are very simple and manageable.

In the OPW one makes a separation (arbitrary to some extent) between core states and outer states (conduction and/or valence states). Corresponding to each atomic core wave function ϕ_c of orbital en-

ergy E_c one forms the Bloch sum

$$\Phi_c(\vec{k}, \vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{\tau}_m} e^{i\vec{k}\cdot\vec{\tau}_m} \phi_c(\vec{r} - \vec{\tau}_m). \quad (1)$$

Valence- and/or conduction-band wave functions are expanded into plane waves

$$W(\vec{k}_m, \vec{r}) = (1/\sqrt{N\Omega}) \exp[i(\vec{k} + \vec{h}_m)\cdot\vec{r}]$$

orthogonalized to the core states. The standard secular equation of the OPW method has the form

$$\left\| \langle W_{\vec{k}_m} | H_{\mathrm{HF}} - E | W_{\vec{k}_n} \rangle \right.$$

$$\left. + \sum_{\mathrm{core}} (E - E_c) \langle W_{\vec{k}_m} | \Phi_c \rangle \langle \Phi_c | W_{\vec{k}_n} \rangle \right\| = 0. \quad (2)$$

The operator H_{HF} is the Hartree-Fock crystalline Hamiltonian

$$H_{\mathrm{HF}} = \frac{\vec{p}^2}{2m} + V_{\mathrm{Coul}} + V_{\mathrm{exch}}, \quad (3)$$

and its expression contains the kinetic energy op-

erator, the electronic and nuclear Coulomb potential, and the electronic exchange potential. In crystals such as argon, composed of closed-shell units, we can assume that the Coulomb and exchange potential of the crystal is the sum of the contributions of the individual atoms. We pass thus to a brief account of HF calculations of the isolated argon atom, in view of their utilization for the HF calculations of the solid.

B. Hartree-Fock calculations for atoms

In the literature first-principles calculations of atoms have been performed extensively using as basis functions either Slater-type orbitals[19] or Gaussian-type orbitals.[20] In the case of argon, we consider the Gaussian representation and adopt as our starting point the HF calculations of Huzinaga,[20] which are summarized for convenience in Table I. The calculations of Huzinaga are practically coincident with the results of Clementi and

TABLE I. Hartree-Fock calculations for the argon atom with Gaussian-type orbitals as basis functions. The $1s$, $2s$, and $3s$ atomic wave functions are expanded on a basis formed by eleven $1s$ GTO's, while $2p$ and $3p$ atomic wave functions are expanded on a basis formed with seven $2p$ GTO's. For convenience the orbital energies, in eV, are also given (after Huzinaga, Ref. 20).

$$\psi_{ns}(\vec{r}) = \frac{2^{7/4}}{\pi^{3/4}} \sum_{i=1}^{11} c_{ni} \alpha_i^{3/4} e^{-\alpha_i r^2} Y_{00}(\vec{r})$$

α_i (a.u.)	ψ_{1s}	ψ_{2s}	ψ_{3s}
4.5654×10^4	1.0039×10^{-3}	2.8432×10^{-4}	-8.8955×10^{-5}
6.9132×10^3	7.6020×10^{-3}	2.1805×10^{-3}	-6.7856×10^{-4}
1.5946×10^3	3.7728×10^{-2}	1.0857×10^{-2}	-3.4139×10^{-3}
4.5730×10^2	1.3725×10^{-1}	4.2372×10^{-2}	-1.3224×10^{-2}
1.5121×10^2	3.3985×10^{-1}	1.1717×10^{-1}	-3.7795×10^{-2}
5.5980×10	4.3554×10^{-1}	2.2328×10^{-1}	-7.2141×10^{-2}
2.2625×10	1.8298×10^{-1}	8.8144×10^{-2}	-3.5457×10^{-2}
7.1177	1.0595×10^{-2}	-5.5957×10^{-1}	2.6328×10^{-1}
2.8287	-1.1900×10^{-3}	-5.5962×10^{-1}	3.8921×10^{-1}
6.3348×10^{-1}	2.9795×10^{-4}	-3.6007×10^{-2}	-6.7844×10^{-1}
2.2525×10^{-1}	-1.4066×10^{-4}	6.7204×10^{-3}	-5.3553×10^{-1}
	$E_{1s} = -3227.21$	$E_{2s} = -335.12$	$E_{3s} = -34.59$

$$\psi_{np} = \frac{2^{11/4}}{\sqrt{3}\,\pi^{1/4}} \sum_{i=1}^{7} c_{ni} \alpha_i^{5/4} r e^{-\alpha_i r^2} \times \begin{cases} Y_{11}(\vec{r}) \\ Y_{10}(\vec{r}) \\ Y_{1-1}(\vec{r}) \end{cases}$$

α_i (a.u.)	ψ_{2p}	ψ_{3p}
2.6878×10^2	1.3568×10^{-2}	-3.7565×10^{-3}
6.3214×10^1	9.2168×10^{-2}	-2.7009×10^{-2}
1.9948×10^1	3.0682×10^{-1}	-8.9052×10^{-2}
7.1087	4.9433×10^{-1}	-1.7027×10^{-1}
2.7159	2.8040×10^{-1}	-9.8686×10^{-3}
7.6352×10^{-1}	1.8778×10^{-2}	5.6312×10^{-1}
2.1992×10^{-1}	-1.7887×10^{-3}	5.5200×10^{-1}
	$E_{2p} = -260.19$	$E_{3p} = -15.88$

Roetti[19] which used eight STO's basis functions; for instance, the orbital energies of argon given in Refs. 20 and 19 differ at most by 0.2 eV.

In the present work we are basically concerned with HF calculations; nevertheless, a few comments on the correlation effects may be of interest. To estimate the correlation energy on the levels of the isolated argon atom, we consider the difference Σ between the computed Hartree-Fock orbital energies $-E$ and the experimental ionization energies I.

The experimental ionization energies of the $3p_{3/2}$ and $3p_{1/2}$ states are $I_{3p_{3/2}} = 15.76$ eV, $I_{3p_{1/2}} = 15.94$ (Ref. 21), with a weighted average $I_{3p} = 15.82$. For the $3s$ state we have $I_{3s} = 29.24$ eV (Ref. 22). For the $2p_{3/2}$ and $2p_{1/2}$ states we have $I_{2p_{3/2}} = 248.63$ eV, $I_{2p_{1/2}} = 250.78$ (Ref. 23), with a weighted averaged $I_{2p} = 249.34$ eV. Comparing the ionization energies with the orbital energies of Table I, we obtain $\Sigma_{3p} = 0.06$ eV, $\Sigma_{3s} = 5.35$ eV, $\Sigma_{2p} = 10.85$ eV; these values of the correlation energies are not significantly changed if one takes into account the relativistic effects[24] due to mass velocity operator and Darwin term. Thus the correlation effects on the argon levels are quite important and for core states are much larger than correlation effects due to the presence of the other atoms in the condensed solid-state phase. These considerations counsel caution in theoretical interpretations of energy thresholds in argon (atom and/or solid), as discussed, for instance, in Ref. 25.

C. Matrix elements of the secular equation

The crystal structure of solid argon is fcc with lattice parameter $a = 10.05$ a.u. The fundamental vectors of the direct and reciprocal lattice are give by $\vec{\tau}_1 = (a/2)(0, 1, 1)$, $\vec{h}_1 = (2\pi/a)(-1, 1, 1)$, and cyclic permutations, respectively.

The ingredients needed for constructing the matrix elements in Eq. (2) are the kinetic operator matrix elements, the orthogonalization terms, the Coulomb-potential Fourier transforms, and the bielectronic exchange integrals. We give here the basic formulas for their analytic evaluation, omitting whenever possible inessential details.

The kinetic operator matrix elements are trivial. The orthogonalization terms are also very simple; we have

$$\langle W_{\vec{k}_m} | \Phi_c \rangle = \frac{1}{N\sqrt{\Omega}} \sum_{\vec{\tau}_m} \int e^{-i(\vec{k}+\vec{h}_m)\cdot\vec{r}} e^{i\vec{k}\cdot\vec{\tau}_m} \phi_c(\vec{r} - \vec{\tau}_m) d\vec{r}$$

$$= \frac{1}{\sqrt{\Omega}} \int e^{-i\vec{k}_m\cdot\vec{r}} \phi_c(\vec{r}) d\vec{r}. \qquad (4a)$$

If ϕ_c is expressed in terms of $1s$ Gaussian func-

tions, we are left with integrals of the type

$$\int e^{-i\vec{k}_m\cdot\vec{r}} e^{-\alpha r^2} d\vec{r} = \left(\frac{\pi}{\alpha}\right)^{3/2} e^{-k_m^2/4\alpha}. \qquad (4b)$$

If ϕ_c is expressed in terms of $2p$ Gaussian functions, we have to consider integrals of the type

$$\int e^{-i\vec{k}_m\cdot\vec{r}} x e^{-\alpha r^2} d\vec{r} = i\frac{\partial}{\partial k_{mx}} \int e^{-i\vec{k}_m\cdot\vec{r}} e^{-\alpha r^2} d\vec{r}$$

$$= \frac{-i}{2\alpha}\left(\frac{\pi}{\alpha}\right)^{3/2} k_{mx} e^{-k_m^2/4\alpha}. \qquad (4c)$$

The use of the derivation technique allows straightforward generalizations to the case of $3d$, $4f$, etc., Gaussian functions. With the aid of the addition theorem of spherical harmonics, one can further simplify the sum on core states in Eq. (2) to a single term for each state with given nl quantum numbers.

We examine now the Fourier transforms of the crystal electronic and nuclear Coulomb potential. Since the crystal potential is taken as the sum of atomiclike potentials we have

$$\langle W_{\vec{k}_m} | V_{\text{Coul}} | W_{\vec{k}_n} \rangle = \frac{1}{\Omega} \int e^{-i(\vec{h}_m-\vec{h}_n)\cdot\vec{r}} V_a(\vec{r}) d\vec{r}$$

$$= \frac{1}{\Omega} V_a(\vec{h}_m - \vec{h}_n). \qquad (5)$$

The electron density distribution $\rho_a(\vec{r})$ for the argon atom is obtained from the wave functions of Table I. The Poisson equation for the potential energy

$$-\nabla^2 V_a(\vec{r}) = 4\pi e^2 \rho_a(\vec{r}) - 4\pi Z e^2 \delta(\vec{r}) \qquad (6a)$$

implies for the Fourier coefficients

$$V_a(q) = \frac{4\pi e^2}{q^2} [\rho_a(q) - Z]. \qquad (6b)$$

Replacing (6b) into (5), we have

$$\langle W_{\vec{k}_m} | V_{\text{Coul}} | W_{\vec{k}_n} \rangle = \frac{4\pi e^2}{\Omega(\vec{h}_m - \vec{h}_n)^2} [\rho_a(|\vec{h}_m - \vec{h}_n|) - Z]. \qquad (7)$$

The Fourier transforms $\rho_a(q)$ are obtained analytically. For reasons of simplicity we here consider only the formulas encountered in the case of a doubly occupied $1s$ Gaussian orbital and fully occupied $2p$ Gaussian orbitals.

A (normalized) $1s$ GTO is given by

$$g_{1s}(\vec{r}) = \frac{2^{7/4}}{\pi^{1/4}} \alpha^{3/4} e^{-\alpha r^2} Y_{00}.$$

Thus

$$\rho(\vec{r}) = 2|g_{1s}(\vec{r})|^2 = 2\left(\frac{2\alpha}{\pi}\right)^{3/2} e^{-2\alpha r^2}$$

and

$$\rho(q) = 2e^{-q^2/8\alpha} . \tag{8}$$

Similarly for a (normalized) $2p$ GTO fully occupied, we have

$$g_{2p}(\vec{r}) = \frac{2^{11/4}}{\sqrt{3}\,\pi^{1/4}} \alpha^{5/4} r\, e^{-\alpha r^2} \times \begin{cases} Y_{11}(\vec{r}) \\ Y_{10}(\vec{r}) . \\ Y_{1-1}(\vec{r}) \end{cases}$$

Thus

$$\rho(\vec{r}) = 2\frac{1}{3}\frac{2^{11/2}}{\pi^{1/2}} \alpha^{5/2} r^2 e^{-2\alpha r^2} \sum_m Y^*_{1m}(\vec{r}) Y_{1m}(\vec{r})$$

$$= \frac{2^{9/2}}{\pi^{3/2}} \alpha^{5/2} r^2 e^{-2\alpha r^2}$$

and

$$\rho(q) = 2\left(3 - \frac{q^2}{4\alpha}\right)e^{-q^2/8\alpha} . \tag{9}$$

Finally we have to consider the bielectronic exchange integrals, involving two Gaussian functions and two plane waves, of the type

$$J_l(\vec{k}_i, \alpha, \beta, \vec{k}_j) = \sum_{m=-l}^{l} \int e^{-i\vec{k}_i \cdot \vec{r}_1} r_2^l e^{-\alpha r_2^2} Y^*_{lm}(\vec{r}_2) \frac{1}{|\vec{r}_1 - \vec{r}_2|} r_1^l e^{-\beta r_1^2} Y_{lm}(\vec{r}_1) e^{i\vec{k}_j \cdot \vec{r}_2} d\vec{r}_1 d\vec{r}_2 . \tag{10}$$

The integrals defined by Eq. (10) are evaluated by means of the auxiliary Dawson function[26]

$$\Phi(x) = \frac{1}{x} e^{-x^2} \int_0^x e^{t^2} dt .$$

For s and p wave functions, we report for completeness the results of Refs. 5 and 6:

$$J_s(\vec{k}_i, \alpha, \beta, \vec{k}_j) = \frac{\pi^{3/2}}{2\alpha\beta(\alpha+\beta)^{1/2}} e^{-(\vec{k}_i - \vec{k}_j)^2/[4(\alpha+\beta)]} \Phi(k\sqrt{\gamma}) , \tag{11}$$

$$J_p(\vec{k}_i, \alpha, \beta, \vec{k}_j) = \frac{3\pi^{3/2}}{8\alpha^2\beta^2(\alpha+\beta)^{1/2}} e^{-(\vec{k}_i - \vec{k}_j)^2/[4(\alpha+\beta)]} \left(\frac{(\vec{k}_i + \vec{k}_j)\cdot\vec{k}}{k^2}[\Phi(k\sqrt{\gamma}) - 1] + \vec{k}_i \cdot \vec{k}_j \Phi(k\sqrt{\gamma}) + 2\gamma\right) , \tag{12}$$

where

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

We have given the tools needed for analytic evaluation of the matrix elements appearing in the Gaussian OPW method, and we are ready to discuss the specific case of solid argon.

III. ENERGY BANDS OF SOLID ARGON

Our computed Hartree-Fock energy bands of solid argon are reported in Fig. 1. The energy levels are labeled following the notations of Koster et al.[27] The crystal energies at some symmetry points are reported in Table II.

The argon atom has the closed-shell electronic configuration $1s^2$, $2s^2 2p^6$, $3s^2 3p^6$; we have considered as core states the K and L levels. We have calculated the band energies at Γ including the first 16 lowest values of $|\vec{h}|$. This means that we have included plane waves up to shell $\langle 442 \rangle$ and $\langle 600 \rangle$, with a total of 259 orthogonalized plane waves. At the other points of the Brillouin zone we have used the same cutoff energy as at Γ. An elevated number of orthogonalized plane waves is necessary in order to give a reliable description also of the $3p$ valence band, as noted by Lipari and Fowler.[4]

We can make a few comments on the energy bands and on the sequence of levels. In corre-

spondence to $1s$, $2s$, and $2p$ atomic states we have core bands. In correspondence to $3s$ and $3p$ atomic states we have a $3s$ band, which bends upward moving from $\vec{k} = 0$, and a $3p$ valence band, which bends downward, as expected by their tight-binding nature. The width of the $3p$ valence band is 1.85 eV in the present calculation, and is in reasonable agreement with the experimental bandwidth[28] of $\simeq 1.7$ eV. Then we have the conduction bands, whose sequence of levels can be understood on the basis of semiqualitative considerations.

For the following speculations, we consider as core states all occupied states, and we analyze qualitatively the OPW secular equation in the perturbative approximation.[8,17] The orthogonalization effects concern only empty lattice states having the same symmetry of core states; the repulsive effects are stronger as core wave functions are larger. In argon, the radial part of the $3p$ wave function is more extended than the $3s$ wave function; this can be seen either from Table I or more simply from the screening parameters $\xi_{3s} = 2.5856$ a.u., $\xi_{3p} = 2.2547$ of the single zeta functions given by Clementi and Roetti.[19] Thus we expect in general that the orthogonalization effects are important for s-like states, are more important for p-like states, and vanish for d-like states and higher angular momentum states.

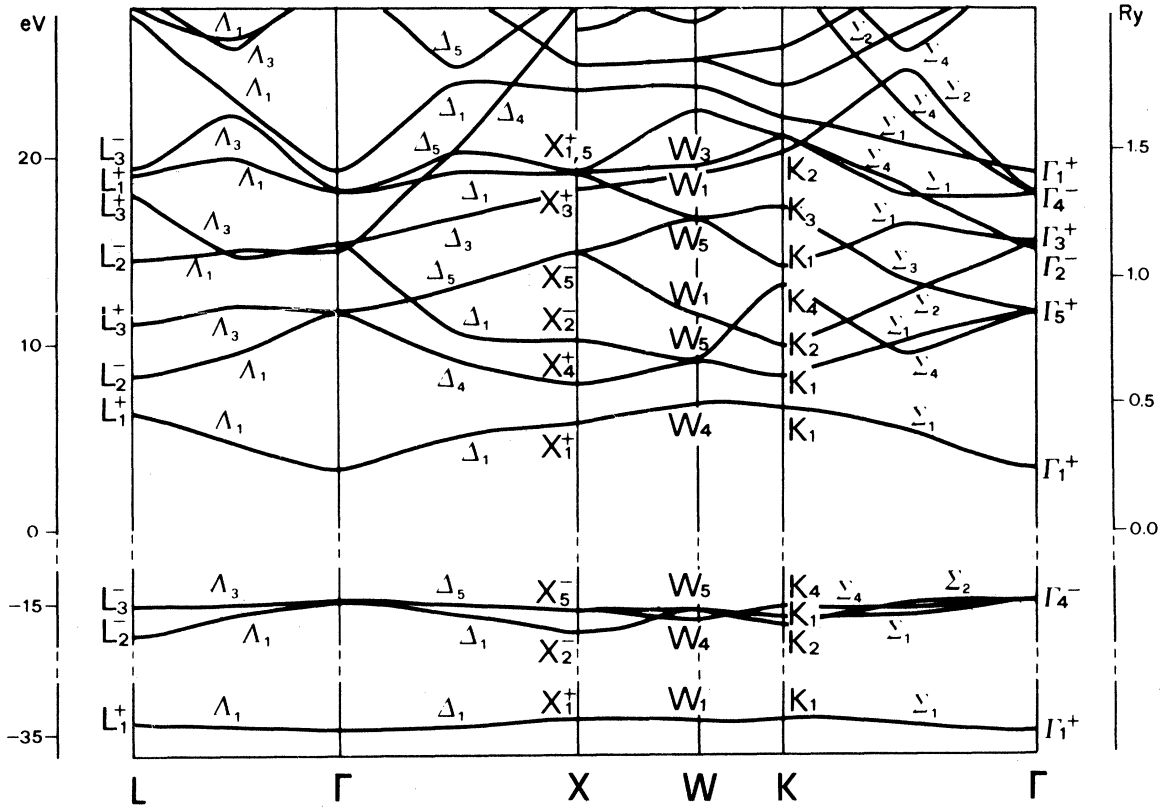Consider, for instance, point Γ. In the empty lattice we have the sequence

FIG. 1. Hartree-Fock energy bands of solid argon.

$$\Gamma_1^+ \ll \Gamma_1^+,\ \Gamma_4^-,\ \Gamma_5^+,\ \Gamma_2^- < \Gamma_1^+,\ \Gamma_3^+,\ \Gamma_4^-,$$

with kinetic energies 0, $(2\pi/a)^2 3$, and $(2\pi/a)^2 4$ rydberg. The state Γ_1^+ is s-like, Γ_4^- is p-like, Γ_5^+ and Γ_3^+ are d-like, Γ_2^- is f-like. The degeneracy of the empty lattice states $\Gamma_1^+,\ \Gamma_4^-,\ \Gamma_5^+,\ \Gamma_2^-$ is removed raising Γ_1^+ and Γ_4^- with respect to $\Gamma_5^+,\ \Gamma_2^-$. Furthermore, the d-like state Γ_3^+, which does not feel orthogonalization effects, has in the crystal an energy lower than that of $\Gamma_1^+,\ \Gamma_4^-$. The expected se-

TABLE II. Energies (in eV) of relevant crystal states in solid argon at the points Γ, X, L, K of the Brillouin zone.

Core states	E_{1s} −3227.21	E_{2s} −335.12		E_{2p} −260.19
3s valence band	Γ_1^* − 34.77	L_1^* − 34.35	X_1^* − 34.22	K_1 − 34.23
3p valence band	Γ_4^- − 14.73	L_2^- − 16.58	X_2^- − 16.45	K_2 − 16.00
		L_3^- − 14.96	X_5^- − 15.32	K_1 − 15.60
				K_4 − 15.11
Conduction states	Γ_1^* 3.20	L_1^* 6.28	X_1^* 5.67	K_1 6.60
	Γ_5^* 11.79	L_2^- 8.28	X_4^* 7.71	K_1 8.18
	Γ_2^- 15.05	L_3^* 11.09	X_2^- 10.33	K_2 9.77
	Γ_3^* 15.28	L_2^- 14.45	X_5^- 15.04	K_4 13.33
	Γ_4^- 17.97	L_3^* 18.14	X_3^* 18.35	K_1 14.09
	Γ_1^* 19.15	L_1^* 19.12	X_5^* 19.28	K_3 17.29

quence of levels at Γ is thus $\Gamma_1^+ \ll \Gamma_5^+ < \Gamma_2^- < \Gamma_3^+$ $< \Gamma_1^+, \Gamma_4^-$, etc., in agreement with the detailed calculations.

At the point X in the empty lattice, we have the sequence X_1^+, X_2^- at energy $(2\pi/a)^2$ rydberg and X_1^+, X_4^+, X_5^- at $(2\pi/a)^2 \, 2$. Among these states only the d-like state X_4^+ does not feel orthogonalization effects. The lowest conduction state at X remains X_1^+ followed by the d-like state X_4^+; then we find X_2^- and X_5^- levels, etc. Similarly, at the point L we have in the empty lattice the levels L_1^+, L_2^- at energy $(2\pi/a)^2 \, \frac{3}{4}$ rydberg, followed by $L_1^+, L_2^-, L_3^+, L_3^-$ at energy $(2\pi/a)^2 \, \frac{11}{4}$. Among these states only L_3^+ does not experience orthogonalization effects; however, the difference of the zero-order energies is large and the empty lattice sequence is maintained for the lower energy levels. We find, in fact, that the lowest conduction state at L is the s-like state L_1^+, followed by the p-like state L_2^-; then we find the d-like state L_3^+, etc.

We wish now to discuss our results in connection with the other calculations available in the literature.

Knox and Bassani[8] opened the investigations on the band structure of argon using a perturbative approximation to the OPW method. Mattheiss[9] used the augmented-plane-wave (APW) method with the Slater free-electron exchange approximation. Rössler[10] applied the Green's-function method with a semiempirical adjustment of the constant in the muffin-tin potential in order to reproduce the ex-

perimental energy gap. Lipari and Fowler[4] and Lipari[12] investigated the energy bands in the HF approximation both with the OPW method and with the mixed basis (MB) method. Dagens and Perrot[11] used the APW method including in a nearly exact way the nonlocal HF exchange potential. Kunz and Mickish[13,14] used a tight-binding formalism with modified localized orbitals. Erre and Resta[15] in their application of the APW method exploited the electron-atom scattering phase shifts calculated in the HF approximation. Finally Khan and Callaway[16] used linear combinations of GTO's with semiempirical modifications of the Slater free-electron exchange approximation.

For a comparison of the results of the various authors we refer to the review article of Rössler.[29] Here we confine our attention to the results of Refs. 11–15, which are strictly of HF type (at least in principle). In Table III we report at the symmetry points Γ, X, L the HF conduction-band energies of argon available in the literature; the notations used are those of Koster et al.[27]

From Table III, we can see the generally satisfactory agreement between our results and those in the literature for the lower conduction states. At higher energies some discrepancy exists among the different authors. Our calculations maintain a reasonable agreement with the APW calculations of Dagens and Perrot,[11] thus justifying the muffin-tin approximation of these authors. For instance, let us consider the energy difference at the point

TABLE III. Hartree-Fock conduction-band energies (eV) in solid argon calculated by several authors.

	Present work	Dagens and Perrot (Ref. 11)	Lipari (OPW—Ref. 12)	Lipari (MB—Ref. 12)	Kunz and Mickish (Ref. 14)	Erre and Resta (Ref. 15)
Γ_1^+	3.20	3.33	2.25	2.41	2.80	2.62
Γ_5^+	11.79	11.65	12.55	12.26	12.9	11.19
Γ_2^-	15.05	15.36	14.29	14.37		
Γ_3^+	15.28	14.66	15.09	15.11	15.7	
X_1^+	5.67	5.91	5.22	5.30	5.80	5.28
X_4^+	7.71	7.92	7.43	7.48	8.47	7.27
X_2^-	10.33	10.19	9.62	9.66	10.6	10.06
X_5^-	15.04	15.11	14.30	14.31	18.2	
L_1^+	6.28	6.49	5.65	5.71	6.57	5.80
L_2^-	8.28	8.11	7.59	7.68	8.66	8.02
L_3^+	11.09	11.04	10.90	10.77	12.6	10.61
L_2^-	14.45	14.70	13.70	13.77		

Γ between s and d conduction bands (Γ_1^+–Γ_5^+ separation). We obtain a separation of 8.59 eV to be compared with the value of 8.32 eV of the APW method.[11] Thus the enigma of the relatively large separation of 10.30 eV of the OPW method of Lipari[12] is removed by the present calculation, which includes exchange in a much simpler way and has a higher number of basis functions. Also the separation between the f-like state Γ_2^- and the d-like Γ_3^+ is in better agreement with the calculations of Dagens and Perrot. We also notice that our conduction-band effective mass at Γ is $m_c^* = 0.54 m_e$; this value as well as the conduction-band shape confirms the reliability of the band parameters used in the interpretation of the valence- and inner-shell excitons in argon (see Ref. 25 and references quoted therein).

Before closing, we make a few comments on the HF energy gap of argon. The HF energy gap in the present calculation is 17.93 eV. Lipari[12] gives an energy gap of 16.39 eV with the MB method and 16.20 eV with the OPW method. Kunz and Mickish[14] and Dagens and Perrot[11] obtain, respectively, an energy gap of 18.5 and 18.52 eV, close to ours. We do not repeat here the considerations and the approaches developed to estimate the correlation effects and justify the correlated energy gap of 14.08 eV, which can be inferred from experiments (see, for instances, Refs. 11, 14, and 25 and references quoted therein).

IV. CONCLUSIONS

In this paper we have examined the possibility of performing first-principles electronic-state calculations using the OPW method and the Gaussian description of the occupied orbitals. The novelty of the GOPW method consists in the fact that the matrix elements of the HF Hamiltonian are constructed analytically. The accuracy of the procedure has been tested with specific reference to solid argon. The approach used should allow wider investigations in the field of first-principles band-structure calculations.

ACKNOWLEDGMENT

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