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Hartree-Fock energy bands in molecular crystals: Solid hydrogen in the cubic phase

Paolo Giannozzi
Institut de Physique Théorique, Université de Lausanne, BSP-Dorigny, CH-1015 Lausanne, Switzerland

Stefano Baroni*
Institut de Physique Théorique, Ecole Polytechnique Fédérale de Lausanne, PHB-Ecublens, CH-1015 Lausanne, Switzerland

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We calculate the Hartree-Fock energy bands of solid hydrogen in the cubic phase, using a plane-wave-basis set. The novelty of our approach is that, by the expression of the crystal density matrix in terms of localized Gaussian functions, all the matrix elements necessary to calculate the energy bands (including those of the nonlocal exchange operator) can be computed in closed analytical form. This is achieved by the extension to molecular crystals of a technique previously applied to solid rare gases. We compare our results with previous theoretical work, and with available experimental data. In particular, we provide a new interpretation of recent photoemission measurements on thick H_2 films deposited on noble metals. The effects of the molecular steric order on the electron states are also briefly discussed.

I. INTRODUCTION

Recently, the availability of sychrotron radiation for spectroscopic purposes has offered new possibilities of investigating the optical properties of molecules and molecular crystals over a wide spectral range.[1] On the theoretical side, not much is known about the electronic states of molecular crystals, and the current understanding of experimental data mainly relies on a critical comparison between the spectra in the gaseous and in the solid phases. The availability of a simple and reliable technique to calculate the energy-band structure of these crystals would be therefore of great interest.

The highly insulating character of molecular crystals makes local-density techniques unsuitable for studying their quasiparticle spectra, and the Hartree-Fock (HF) method is a better starting approximation in this case. It is known, in fact, that any local approximation to the exchange potential leads to a severe underestimate of the optical gap,[2] and no assessed method to improve the local-density results is presently at hand.[3] The Hartree-Fock approximation, on the contrary, systematically overestimates the optical gap.[4] In wide-gap insulators, however, the correlation effects omitted by the HF approximation are comparatively small and can be managed to a reasonable degree of reliability by a variety of methods.[4]

In molecular crystals, the density matrix necessary to set up the Fock operator is conveniently expressed in terms of free molecular orbitals.[5] On the other hand, while occupied orbitals can be satisfactorily described by a basis of a few localized functions per atom, the proper description of virtual orbitals requires a much more flexible basis set. The joint use of a local-orbital expression for the crystal density matrix and of an orthogonalized-plane-wave (OPW) set for describing *both* valence and conduction bands, has proved to be a valuable tool for HF calculations in rare-gas solids.[6,7] One major difficulty of OPW-HF calculations in solids is due to the nonlocal character of the exchange potential which can make the computation of its matrix elements rather cumbersome.[6] In a series of recent papers,[7] it has been shown that whenever the crystal potential can be satisfactorily expressed as a sum of atomic potentials, these difficulties can be overcome by expressing the atomic density matrix in terms of Gaussian-type orbitals (GTO). When this is done, all the matrix elements occurring in the OPW calculation can be computed in closed analytical form. This technique has been also successfully applied to correlated energy-band calculations in the Coulomb-hole—plus—screened-exchange (COHSEX) approximation.[8]

In this paper we consider the case where the crystal density matrix cannot be expressed any longer as a sum of atomic terms, and interatomic contributions to the Fock operator play an important role. In the case of molecular crystals, such contributions from atoms within the same molecule (intramolecular contributions) are of course very important, while those coming from atoms belonging to different molecules (intermolecular terms) are far smaller. The latter, however, are known to affect the valence bands of these crystals in a non-negligible way.[9,10] We propose a technique to deal with these interatomic contributions to the crystal potential within the OPW method, and we apply it to solid hydrogen in the cubic phase. In this case, no core states are present, and we use a plane-wave-basis set. For the purposes of the present paper, we have found it convenient to apply this technique to intramolecular terms only, while intermolecular ones are accounted for by a simple perturbation formula based on the work by Gilbert and Kunz.[11] The simplicity of solid H_2 and the existence of other theoretical works on the electronic states of this crystal make it possible to compare our approach with the others found in the literature. The effects of the molecular steric order on the electron states will be briefly discussed and the results compared with available absorption and photoemission data.

II. HARTREE-FOCK APPROXIMATION IN MOLECULAR CRYSTALS

A. General consideration

The Hartree-Fock equation for a crystal reads:

$$F\phi(\vec{k},\vec{r})\equiv\left[-\frac{\hbar^2}{2m}\nabla^2+V_{\text{nucl}}(\vec{r})+e^2\int\frac{\rho(\vec{r}'\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}'\right]\phi(\vec{k},\vec{r})-\frac{e^2}{2}\int\frac{\rho(\vec{r},\vec{r}')}{|\vec{r}-\vec{r}'|}\phi(\vec{k},\vec{r}')d\vec{r}'=\epsilon(\vec{k})\phi(\vec{k},\vec{r})\ , \tag{1}$$

where V_{nucl} is the nuclear potential, $\rho(\vec{r},\vec{r}')$ the spin-independent (Dirac) density matrix, and F the Fock operator of the crystal. According to Löwdin,[5] the density matrix of a system made up of closed-shell units (which will be referred to as "molecules," but could also be atoms or ions) can be approximately expressed in terms of free molecular orbitals $\{\varphi_i\}$:

$$\rho(\vec{r},\vec{r}')\simeq 2\sum_{i,j}(S^{-1})_{ij}\varphi_i(\vec{r})\varphi_j^*(\vec{r}')\ , \tag{2}$$

where the indices i and j label molecular quantum numbers and positions, and S^{-1} is the inverse of the overlap matrix:

$$S_{ij}=\langle\varphi_i\,|\,\varphi_j\rangle\equiv\delta_{ij}+\Delta_{ij}\ .$$

In molecular crystals, the overlap between neighboring molecular orbitals is small (~ 0.01); in this case, S^{-1} can be evaluated to first order in Δ, and one obtains

$$(S^{-1})_{ij}\simeq\delta_{ij}-\Delta_{ij}\ .$$

In most cases of interest Δ_{ij} is non-negligible only for nearest-neighbor molecules, and the following approximate expression for $\rho(\vec{r},\vec{r}')$ holds:

$$\rho(\vec{r},\vec{r}')\simeq 2\sum_{i}\varphi_i(\vec{r})\varphi_i^*(\vec{r}')-2{\sum_{i,j}}^{I}S_{ij}\varphi_i(\vec{r})\varphi_j^*(\vec{r}')\ , \tag{3}$$

where $\sum^I$ indicates a sum running over couples of nearest-neighbor molecules. Accordingly, we define an "intramolecular" Fock operator F_0 as the sum of the kinetic operator plus free-molecular potentials [cf. first term of the density matrix (3)]. The contribution to F of the second term in Eq. (3) will be denoted by ΔF ("intermolecular" contribution).

The only nontrivial step in the evaluation of the matrix elements between plane waves of the Fock operator corresponding to the density matrix (2) is the calculation of bielectronic integrals of the type

$$J=\int d\vec{r}_1d\vec{r}_2e^{-i\vec{k}_1\cdot\vec{r}_1}\varphi_i^*(\vec{r}_2)\frac{1}{r_{12}}e^{i\vec{k}_2\cdot\vec{r}_1}\varphi_j(\vec{r}_2)\ , \tag{4a}$$

$$K=\int d\vec{r}_1d\vec{r}_2e^{-i\vec{k}_1\cdot\vec{r}_1}\varphi_i^*(\vec{r}_2)\frac{1}{r_{12}}e^{i\vec{k}_2\cdot\vec{r}_2}\varphi_j(\vec{r}_1)\ . \tag{4b}$$

In Ref. 7, a technique for evaluating the above integrals was provided, in the case where both the φ's were atomic functions centered on a same site. In the following we extend these results to the general case of functions centered on different sites.

B. Calculation of matrix elements

Restricting ourself to localized orbitals of s-like symmetry, we define

$$J_s(\vec{k}_1,\alpha_1,\vec{\delta}_1;\vec{k}_2,\alpha_2,\vec{\delta}_2)\equiv\int d\vec{r}_1d\vec{r}_2e^{-i\vec{k}_1\cdot\vec{r}_1}e^{-\alpha_1(\vec{r}_2-\vec{\delta}_1)^2}\frac{1}{r_{12}}e^{i\vec{k}_2\cdot\vec{r}_1}e^{-\alpha_2(\vec{r}_2-\vec{\delta}_2)^2} \tag{5a}$$

and

$$K_s(\vec{k}_1,\alpha_1,\vec{\delta}_1;\vec{k}_2,\alpha_2,\vec{\delta}_2)\equiv\int d\vec{r}_1d\vec{r}_2e^{-i\vec{k}_1\cdot\vec{r}_1}e^{-\alpha_2(\vec{r}_2-\vec{\delta}_2)^2}\frac{1}{r_{12}}e^{i\vec{k}_2\cdot\vec{r}_2}e^{-\alpha_1(\vec{r}_1-\vec{\delta}_1)^2}\ . \tag{5b}$$

The product of two GTO's centered on different sites may be expressed as a single GTO centered on a third site.[12] J_s is thus simply the Fourier transform of the electrostatic potential generated by a Gaussian charge distribution. The final result is

$$J_s=e^{-\alpha_{12}\Delta_{12}^2}e^{-i\vec{k}_{12}\cdot\vec{\delta}_{12}}\frac{4\pi}{k_{12}^2}\left[\frac{\pi}{\alpha_1+\alpha_2}\right]^{3/2}e^{-k_{12}^2/4(\alpha_1+\alpha_2)}\ , \tag{6}$$

where

$$\vec{\Delta}_{12}=\vec{\delta}_1-\vec{\delta}_2,\ \ \alpha_{12}=\frac{\alpha_1\alpha_2}{\alpha_1+\alpha_2},\ \ \delta_{12}=\frac{\alpha_1\vec{\delta}_1+\alpha_2\vec{\delta}_2}{\alpha_1+\alpha_2},\ \ \vec{k}_{12}=\vec{k}_1-\vec{k}_2\ .$$

A technique to evaluate analytically the exchange integral K_s is presented in Ref. 7, in the case where $\vec{\delta}_1=\vec{\delta}_2$. Proceeding along lines similar to those of Refs. 7 and 13, we examine now the general case $\vec{\delta}_1\neq\vec{\delta}_2$. We first decouple $\vec{r}_1$ and $\vec{r}_2$ by Fourier analyzing $1/r_{12}$, and then integrate with respect to $\vec{r}_1$ and $\vec{r}_2$:

$$K_s(\vec{k}_1,\alpha_1,\vec{\delta}_1;\vec{k}_2,\alpha_2,\vec{\delta}_2)=\frac{\pi}{2(\alpha_1\alpha_2)^{3/2}}e^{-i(\vec{k}_1\cdot\vec{\delta}_1-\vec{k}_2\cdot\vec{\delta}_2)}\int e^{i\vec{q}\cdot\vec{\Delta}_{12}}\exp\left[-\frac{(\vec{q}-\vec{k}_1)^2}{4\alpha_1}-\frac{(\vec{q}-\vec{k}_2)^2}{4\alpha_2}\right]\frac{1}{q^2}d\vec{q}$$

$$=\frac{\pi}{2(\alpha_1\alpha_2)^{3/2}}e^{-i(\vec{k}_1\cdot\vec{\delta}_1-\vec{k}_2\cdot\vec{\delta}_2)}e^{-(k_1^2/4\alpha_1)-(k_2^2/4\alpha_2)}\int e^{-(q^2/4\alpha_{12})}e^{i\vec{q}\cdot\vec{\kappa}}\frac{1}{q^2}d\vec{q}\ ,$$

where

$$\vec{\kappa}=\vec{\Delta}_{12}-i\left[\frac{\vec{k}_1}{2\alpha_1}+\frac{\vec{k}_2}{2\alpha_2}\right]$$

is a complex vector. To perform the angular integration, we observe that, if $\vec{\kappa}$ were real, the spherical average of $e^{i\vec{q}\cdot\vec{\kappa}}$ would be $\sin(q\kappa)/q\kappa$. By analyticity, the same result must hold for complex $\vec{\kappa}$. We have then

$$K_s=\frac{2\pi^2}{(\alpha_1\alpha_2)^{3/2}}e^{-i(\vec{k}_1\cdot\vec{\delta}_1-\vec{k}_2\cdot\vec{\delta}_2)}e^{-(k_1^2/4\alpha_1)-(k_2^2/4\alpha_2)}\int_0^\infty e^{-(q^2/4\alpha_{12})}\frac{\sin(q\kappa)}{q\kappa}dq\ ,$$

where $\kappa=(\vec{\kappa}\cdot\vec{\kappa})^{1/2}$. The above integral can be expressed in terms of the error function of complex argument,[14] and the final result is

$$K_s=\frac{\pi^3}{(\alpha_1\alpha_2)^{3/2}}e^{-i(\vec{k}_1\cdot\vec{\delta}_1-\vec{k}_2\cdot\vec{\delta}_2)}e^{-(k_1^2/4\alpha_1)-(k_1^2/4\alpha_2)}\frac{\mathrm{erf}[\kappa(\alpha_{12})^{1/2}]}{\kappa}\ . \tag{7}$$

With the help of a standard computer routine for the complex error function,[15] the numerical evaluation of K_s is straightforward. The method presented here for s-like localized functions can be easily extended by differentiation to the general case of higher angular momentum, and it is therefore applicable to more complex molecular crystals than solid H_2.

C. Evaluation of Intermolecular terms

The technique revealed above applies to intramolecular as well as to intermolecular contributions to the Fock operator. However, the effects of the latter are comparatively small, and their computation is time consuming. For this reason, we give here a simple prescription, based on an approximation by Gilbert and Kunz,[11] to treat their effects separately. To this end, we direct attention for a moment to a local-orbital description of the energy bands. Retaining only terms which are linear in the overlap, we neglect all the matrix elements of ΔF between molecular orbitals on the same site, and between orbitals which are not both occupied in the free molecule. For occupied orbitals $\varphi_A(\vec{r}-\vec{d}_A)$, and $\varphi_B(\vec{r}-\vec{d}_B)$, one has[11]

$$\langle\varphi_A\,|\,\Delta F\,|\,\varphi_B\rangle\simeq S_{AB}\frac{e^2}{|\,\vec{d}_A-\vec{d}_B\,|}\ . \tag{8}$$

For the sake of simplicity, we consider a crystal with one molecule per unit cell, giving rise to an s-like valence band. This is the case of solid H_2, when the relative orientations of the molecules are disregarded. The extension to more complicated cases is straightforward. According to Eq. (8), the correction to the linear-combination-of-molecular-orbitals (LCMO) valence band is given, to first order in S, by

$$\Delta\epsilon_v(\vec{k})\simeq S_{0,\vec{\tau}_I}\frac{e^2}{|\,\vec{\tau}_I\,|}\sum_{\vec{\tau}_I}e^{ik\cdot\vec{\tau}_I}\ , \tag{9}$$

where $\vec{\tau}_I$'s are nearest-neighbor translation vectors. In the same approximation, conduction bands are unaffected by ΔF.

A similar conclusion could also be obtained in the plane-wave formalism. We neglect the Coulomb integrals J due to molecular orbitals on different sites (whose effect is second order in S), and treat the corresponding exchange integrals by the following approximation:

$$K_s(\vec{k}_1,\alpha_1,\vec{\delta}_1;\vec{k}_2,\alpha_2,\vec{\delta}_2)\simeq\frac{\pi^3}{(\alpha_1\alpha_2)^{3/2}}\frac{1}{|\,\vec{\delta}_1-\vec{\delta}_2\,|}e^{-i(\vec{k}_1\cdot\vec{\delta}_1-\vec{k}_2\cdot\vec{\delta}_2)}e^{-(k_1^2/4\alpha_1)-(k_2^2/4\alpha_2)}\ . \tag{10}$$

The corresponding first-order correction to a given energy band is given by

$$\Delta\epsilon(\vec{k})\simeq S_{0,\vec{\tau}_I}\frac{e^2}{|\tau_I|}\,|\langle\phi_0^v(k)\,|\,\phi(k)\rangle|^2\sum_{\vec{\tau}_I}e^{i\vec{k}\cdot\vec{\tau}_I}\;, \qquad (11)$$

where $\phi(\vec{k})$ is the unperturbed wave function of the band under consideration, and $\phi_0^v(\vec{k})$ is the Bloch sum made up by *free* molecular orbitals. The above approximations were tested against detailed calculations on a model fcc He crystal.[16] Several values of $S_{0,\vec{\tau}_I}$ were considered upon variation of the lattice constant. For the values of $S_{0,\vec{\tau}_I}$ of interest in the study of molecular crystals, the approximations (9)—(11) proved to be very good. Calculations were made (i) using formula (9), (ii) using formula (11), (iii) inserting the approximation (10) directly into the matrix elements of the Fock operator, and (iv) avoiding any approximation either on the calculation of the matrix elements or on the inversion of the overlap matrix.[17] Since the results so obtained coincided within a few hundreths of an eV, we decided to adopt the simplest approach, i.e., to correct the valence energy bands perturbatively by Eq. (9).

III. ENERGY BAND STRUCTURE IN SOLID HYDROGEN

A. General considerations

The crystal structure of solid hydrogen at very low temperature is described by the space group $Pa3$ (T_h^6).[18,19] The translational symmetry is simple cubic, and each unit cell contains four molecules, whose centers of mass form an fcc lattice, and whose axis are oriented along the four-body diagonals of the cube. The lattice parameter is $a_0=10.04$ a.u., and the interatomic distance within a same molecule is $d=1.40$ a.u., as in the free molecule.[18(c)] The molecular orbitals used to set up the crystal Hamiltonian have been calculated self-consistently for the free molecule using the $(6s)$ even-tempered GTO basis set proposed by Schmidt and Ruedenberg.[20] The molecular total energy and $1\sigma_g$ orbital energy so found are -30.70 and -16.21 eV, respectively. The overlap between nearest-neighbor molecules is independent of the relative orientation, and its value is $S=1.15\times10^{-2}$.

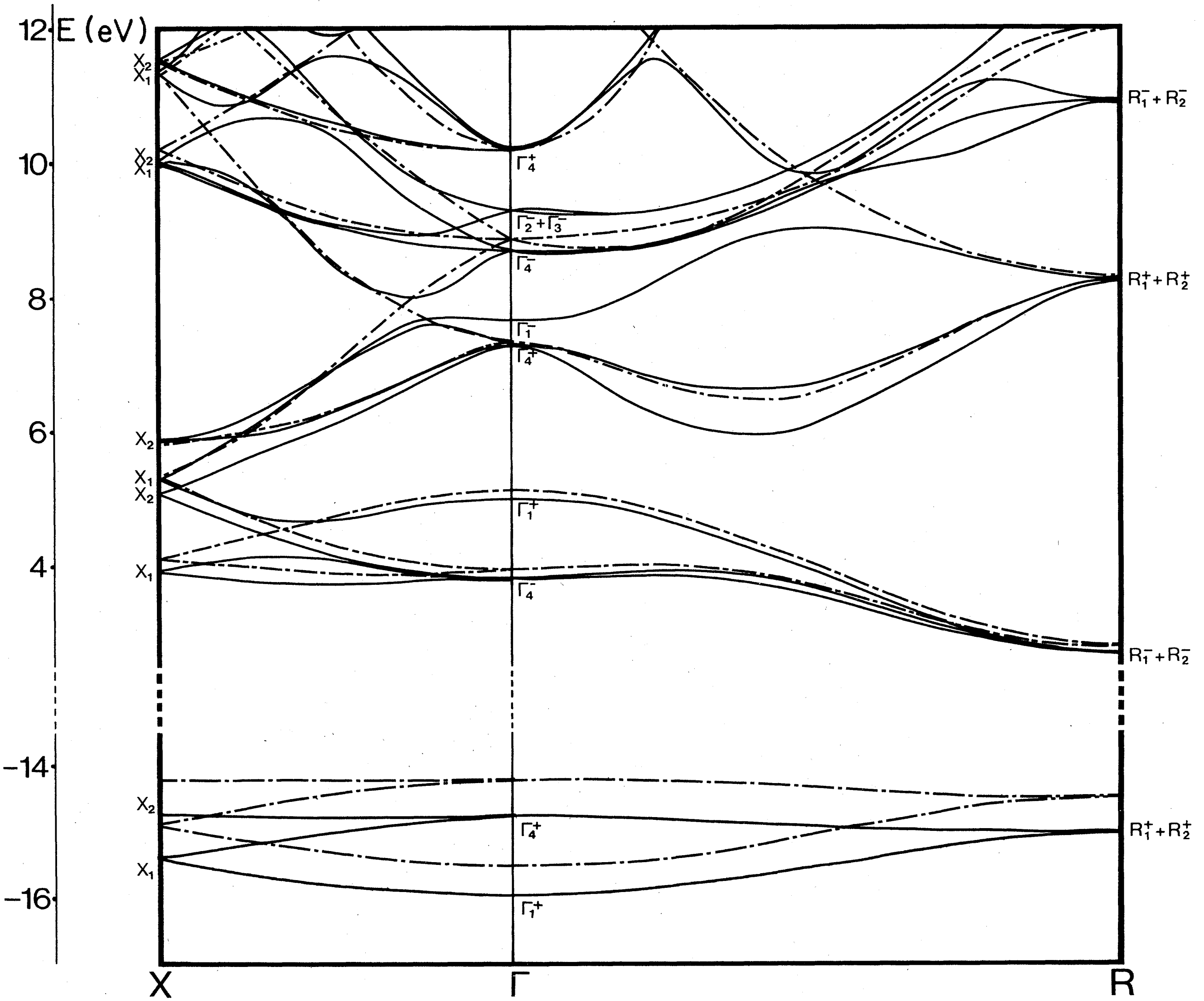

FIG. 1. Hartree-Fock energy bands in cubic solid H_2. Solid lines, $Pa3$ results; dashed lines, fcc results (see text).

B. Numerical results and discussion

We display in Fig. 1 the calculated energy bands of solid hydrogen. Solid lines refer to energy bands obtained taking into account the steric order of the molecules, while dashed lines are the results of a calculation in which the molecular potential has been averaged with respect to the four possible orientations of the molecule in the unit cell. We will refer to the former as *Pa*3, and to the latter as fcc results. The energy cutoff for the construction of the plane-wave-basis set has been set to $24(2\pi\hbar/a_0)^2$. At point Γ, this amounts to including plane waves up to wave vectors of the type (4,2,2). The maximum number of such plane waves is 485 and 137 in the *Pa*3 and fcc cases, respectively. Intermolecular contributions to the crystal potential have been accounted for by Eq. (9), as explained in Sec. II C. In the fcc case, we have also calculated the energy bands with an energy cutoff of $43(2\pi\hbar/a_0)^2$, and verified that all the eigenvalues of Fig. 1 were converged better than 0.1 eV. In Table I we report the results of such fcc calculations.

A comparison of the *Pa*3 and fcc results shows that the effect of the molecular steric order on the electronic energy levels is practically negligible for conduction bands, while it shifts almost rigidly the valence bands by 0.5 eV downwards. As optical experiments are performed at temperatures near the onset of an order-disorder transition,[18,21] the fluctuations in the orientational ordering may be very important. We suggest, therefore, that experimental data should be compared with fcc calculations, which better describe an average disordered situation and which are by far less time consuming than *Pa*3 ones.

The absorption spectrum of solid H_2 for $\hbar\omega < 20$ eV schematically consists of two broad structures peaking at about 12.5 and 17 eV,[21] the first of which has been interpreted as due to excitonic effects.[21,22] The HF fundamental gap corresponds to an $L_1^+ \to L_2^-$ transition (in the notation appropriate to the fcc "average" crystal) and is of 17.3 eV. The effect of electronic correlation on the energy bands of an insulating crystal is to shift almost rigidly the valence bands upwards and the conduction bands downwards.[6-8,23] The reduction of the energy gap E_g due to correlation effects ($E_g^{\mathrm{HF}} - E_g^{\mathrm{expt}} = \Delta E_g$) can be divided in a first approximation into a free-molecule contribution ΔI and a host contribution P. The former is the difference between the experimental ionization potential of the free molecule and the corresponding calculated orbital energy; the latter is due to the polarization of the neighboring molecules, and is of the order of the Mott-Littleton energy E_{ML}:[23,24]

$$P \simeq E_{\mathrm{ML}} \equiv e^2 \left[1 - \frac{1}{\epsilon_s} \right] \frac{6.3346}{\pi d_0} \,,$$

where ϵ_s is the static dielectric constant of the crystal. In solid rare gases, E_{ML} is found to account for 60–70 % of P.[6-8,23] The static dielectric constant of solid H_2 at zero temperature has been calculated by extrapolating the known value for liquid hydrogen at $T = 20$ K (Ref. 25) by means of the Clausius-Mossotti formula, and found to be $\epsilon_s = 1.3$: The corresponding value of E_{ML} is 1.3 eV. The ionization potential of the free molecule is 15.5 eV,[26] which, together with the calculated $1\sigma_g$ orbital energy previously mentioned, gives a value of 0.7 eV for ΔI. The resulting ΔE_g ($\sim$2.0–2.5 eV) lowers the gap to $\sim$15 eV, in substantial agreement with previous estimates based on experimental data.[21(d),21(e)] Further information about the static dielectric function of solid $\mathrm{H_2}$ would be valuable in order to better account for correlation effects on the energy bands, e.g., in the COHSEX approximation. According to our results, we conclude that the absorption band at 12.5 eV is due to excitonic effects, while the one at 17 eV is due to density-of-states effects in the band-to-band transitions. Our conclusions differ from previous theoretical investigations based on the local-density approximation[27] on an intermediate-neglect-of-differential-overlap (INDO)-type cluster approximation,[28] or on the "dielectric approach" to the crystal potential.[29] The energy gap predicted by these calculations ranges from 9 to 11 eV, ruling out the interpretation of the first absorption band of solid $\mathrm{H_2}$ as due to excitonic effects. The absence of excitonic effects in the absorption spectrum of such a highly insulating crystal as solid $\mathrm{H_2}$ would be rather surprising, and a comparison of the spectra in the gaseous and solid phases further confirms the excitonic nature of the first absorption band of this crystal.[21(e)]. These considerations confirm that an accurate treatment of the exchange operator is essential in order to obtain band gaps in good agreement with experiments. The comparatively better value of the band gap obtained in Ref. 10 is due to the use of the X_α method. The α value was fixed in such a way to reproduce the *exact* exchange matrix element between two plane waves at $\vec{k} = \vec{0}$.

TABLE I. Hartree-Fock energy bands of cubic solid $\mathrm{H_2}$ in the fcc approximation (see text). Units are eV.

Γ	X	L	W	K
-15.61 Γ_1^+	-14.39 X_1^+	-14.66 L_1^+	-14.37 W_1	-14.41 K_1
5.06 Γ_1^+	3.94 X_2^-	2.79 L_2^-	5.33 W_5	4.63 K_2
13.28 Γ_4^-	7.32 X_1^+	8.26 L_1^+	5.81 W_4	4.95 K_1
15.38 Γ_5^+	8.85 X_5^-	12.01 L_3^-	13.29 W_1	9.04 K_1
15.75 Γ_2^-	10.18 X_4^+	14.16 L_3^+	14.90 W_4	9.51 K_4
19.44 Γ_1^+	20.26 X_1^-	14.30 L_2^-	16.32 W_5	14.77 K_1
20.01 Γ_4^-		21.63 L_1^+	23.10 W_1	17.54 K_1
				20.05 K_4

As concerns the valence band, we predict a bandwidth of 1.2 eV, while the top of the band is at -14.4 eV (X_1^+). Previous experience has shown that, at least for narrow bands, the valence-band width is well predicted in the HF approximation.[8] According to our results, the ionization potential of solid H_2 should be located at $I_P \simeq -E(X_1^+) - \Delta I - \frac{1}{2}E_{\rm ML} = 13.0$ eV. Here again, our results disagree from those obtained in the local-density or "dielectric" schemes which predict a smaller bandwidth and a much smaller binding energy. The bandwidths obtained by the LCMO method[10,30] are also sensibly smaller than our own. This is probably due to the lack of flexibility of the LCMO basis set and to the fact that, in molecular crystals, the hopping integrals responsible for the spread in the valence-band energies are very sensitive to the tails of the molecular orbitals, which are poorly described by approximate wave functions.

Unfortunately, there are no photoemission data on bulk solid H_2 to which compare our predictions for the valence band. Our results, however, are compatible with the photoemission measurements on thick H_2 layers deposited on Cu or Au, by Eberhardt *et al.*[31] In the case of Cu, the photoemission spectrum reported by these authors consists of a typical photoemission band of the substrate followed by a second structure characterized by a binding energy $E_b = 10.4$ eV, and a width $\Delta_v = 2.1$ eV, which has been interpreted as due to bandlike states of the deposited layers. Assuming a work function $W = 4.4$ eV, this interpretation implies a width of the valence band of solid H_2 equal to Δ_v, and an ionization potential $I_P = E_b + W - \frac{1}{2}\Delta_v = 13.7$ eV. Similar conclusions may be drawn in the case of Au. These values are in fair agreement with those calculated in the present paper ($\Delta_v = 1.2$, $I_P = 13.0$ eV). The larger value of the observed "valence-band width" is probably due to broadening interactions with the substrate, while the larger "ionization potential" could be the consequence of a less efficient screening of the hole state, with respect to bulk solid H_2. Eberhardt *et al.*, who according to previous calculations assumed a band gap of 10 eV, were rather surprised to find the Fermi level coinciding just about with the bottom of the conduction band of solid H_2, and had to invoke a charge transfer from the substrate into the H_2 film in order to account for such a situation. According to our results, no such mechanism should be invoked since the energy gap obtained (~ 15 eV) allows the location of the Fermi level at midgap, as one expects.

IV. CONCLUSIONS

In the present paper, we have shown that reliable information about the electronic states of molecular crystals can be obtained by means of HF calculations within the (orthogonalized) plane-wave method. The combined use of GTO's for describing the crystal density matrix and of plane waves (orthogonalized to core states, if necessary) for describing valence and conduction bands makes the problem numerically tractable.

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*Present address: Instituto di Fisica Teorica, Universita di Trieste, Trieste, Italy.

[1] See, for instance, E. E. Koch and B. F. Sonntag, in *Synchrotron Radiation,* edited by C. Kunz (Springer, Heidelberg, 1979); E. E. Koch and P. Gurtler, in *Photophysics and Photochemistry in the Vacuum Ultraviolet,* edited by G. Findley, S. McGlynn, and R. Huebner (Reidel, Dordrecht, 1983).

[2] See, for instance, A. Zunger, J. P. Perdew, and G. L. Oliver, Solid State Commun. **34**, 933 (1980).

[3] For a review on density-functional approximation in solids, see, A. R. Williams and U. von Barth, in *Theory of the Inhomogeneous Electron Gas,* edited by N. H. March and S. Lundqvist (Plenum, New York, 1983). For a recent attempt to go beyond the local-density approximation in semiconductors, see F. Manghi, G. Riegler, C. M. Bertoni, C. Calandra, and G. B. Bachelet, Phys. Rev. B **28**, 6157 (1983).

[4] See, for instance, S. T. Pantelides, D. J. Mickish, and A. B. Kunz, Phys. Rev. B **10**, 2602 (1974), and references quoted therein.

[5] P. O. Löwdin, Adv. Phys. **5**, 1 (1956).

[6] N. O. Lipari and W. B. Fowler, Phys. Rev. B **2**, 3454 (1970).

[7] G. Grosso and G. Pastori Parravicini, Phys. Rev. B **20**, 2366 (1979); S. Baroni, G. Grosso, and G. Pastori Parravicini, *ibid.* **23**, 6441 (1981); S. Baroni, G. Grosso, and G. Pastori Parravicini, Phys. Status Solidi B **110**, 227 (1982).

[8] S. Baroni, G. Grosso, and G. Pastori Parravicini, Phys. Rev. B **29**, 2891 (1984).

[9] A. B. Kunz, Phys. Rev. B **9**, 5330 (1974); L. Piela, L. Pietronero, and R. Resta, *ibid.* **9**, 5332 (1974).

[10] G. Pastori Parravicini, I. Villa, and M. Vittori, Phys. Status Solidi B **67**, 345 (1975).

[11] T. L. Gilbert, in *Sigma Molecular Orbital Theory,* edited by O. Sinanoglu and B. Weiberg (Yale University Press, New Haven, 1969); A. B. Kunz, Phys. Status Solidi B **36**, 301 (1969).

[12] I. Shavitt, in *Methods in Computational Physics,* edited by B. Alder, S. Fernbach, and M. Rotenberg (Academic, New York, 1963), Vol. 2.

[13] N. E. Brener and J. L. Fry, Phys. Rev. B **17**, 506 (1978).

[14] *Tables of Integral Transforms,* edited by A. Erdely (McGraw-Hill, New York, 1954), Vol. 1, p. 73, no. 21.

[15] W. Gautschi, Algorithm 363, Commun. ACM **16**, 635 (1969). A FORTRAN translation of the above ALGOL procedure is filed in the CERN program library.

[16] G. Pezzica, S. Baroni, and P. Giannozzi (unpublished).

[17] G. Grosso, G. Pastori Parravicini, and R. Resta, Phys. Status Solidi B **73**, 371 (1976).

[18] (a) M. Clouter and H. P. Gush, Phys. Rev. Lett. **15**, 200 (1965); (b) K. F. Mucker, S. Talhouk, P. M. Harris, and D. White, *ibid.* **15**, 586 (1965); (c) R. L. Mills and A. F. Schuch, *ibid*, **15**, 722 (1965); (d) J. Felsteiner, *ibid*, **15**, 1025 (1965).

[19] A. F. Schuch, R. L. Mills, and D. A. Depatie, Phys. Rev. **165**,

1032 (1968); H. Moraal, Phys. Status Solidi B **50**, 327 (1972); R. J. Lee and J. C. Raich, Phys. Rev. B **5**, 1591 (1972).

[20] M. W. Schmidt and K. Ruedenberg, J. Chem. Phys. **71**, 3951 (1979).

[21] (a) G. Baldini, Jpn. J. Appl. Phys. Suppl. 1 **4**, 613 (1965); (b) A. Gedanken, B. Raz, and J. Jortner, Chem. Phys. Lett. **14**, 326 (1972); (c) L. Schmidt, Phys. Lett. **36A**, 87 (1971); (d) A. Gedanken, B. Raz, and J. Jortner, J. Chem. Phys. **59**, 2752 (1973); (e) K. Inoue, H. Hanzaki, and S. Suga, Solid State Commun. **30**, 627 (1979).

[22] W. Andreoni and L. Resca, Nuovo Cimento B **39**, 524 (1977).

[23] W. B. Fowler, Phys. Rev. **221**, 657 (1966).

[24] G. Grosso, L. Martinelli, and G. Pastori Parravicini, Solid State Commun. **25**, 435 (1978).

[25] *Handbook of Chemistry and Physics,* edited by R. C. Weast (CRC, Boca Raton, 1980).

[26] K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Norstrand, New York, 1979).

[27] R. Monnier, E. L. Pollock, and C. Friedli, J. Phys. C **7**, 2467 (1974).

[28] A. Zunger, J. Phys. Chem. Solids **36**, 229 (1975).

[29] C. Friedli and N. W. Ashcroft, Phys. Rev. B **16**, 662 (1977).

[30] L. A. Gomez, G. Pastori Parravicini, L. Resca, and R. Resta, J. Phys. C **6**, 1926 (1973).

[31] W. Eberhardt, R. Cantor, F. Greuter, and E. W. Plummer, Solid State Commun. **42**, 799 (1982).