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THE USE OF WANNIER FUNCTION IN THE CALCULATIONS  
OF BAND STRUCTURE OF COVALENT CRYSTALS \* *CM*

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ABSTRACT

A variational procedure has been used to build up Wannier functions to study the energy bands of diamond, silicon and  $\alpha$ -tin. For the case of silicon the Wannier function, density of charge and band structure are calculated self-consistently and a simple method in a non-self-consistent way has been used to compute the band structure of diamond, silicon and  $\alpha$ -tin. The method seems to be effective to describe the electronic properties of covalent crystals.

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I. INTRODUCTION

The interest in the problems of vacancies, impurities and surfaces has revived the use of localized functions in the study of the electronic structure of solids. The Wannier function seems to be very suitable to deal with the description of electron in a covalent crystal. Koster<sup>1)</sup> and Parzen<sup>2)</sup> have proved some important properties of the Wannier function (WF), respectively. In order to obtain the WF, it is necessary for the Bloch function to be specified in detail and to be integrated over the Brillouin zone. These are the difficulties which have precluded the use of WF as the basis in quantitative study of electronic states in solids. The early study has been done by Wainwright and Parzen<sup>3)</sup>, they applied the WF to calculate the energy band of lithium (Li). Their result can be comparable with that due to the OPW method.

Kohn<sup>4)</sup> has provided a variational procedure for building up WF from a set of localized function  $f_m(\vec{r}, \beta)$  with some variational parameters  $\beta$ . Since then, Andreoni<sup>5)</sup> has performed the calculation of band structure of metallic hydrogen giving the result quite near to that given by the KKR method. Kane and Kane<sup>6)</sup> have made a computation of the valence bands of silicon with WF built up from Gaussian type orbitals (GTO), but they do not provide a self-consistent picture. Soon after, Tejedor and Vergés<sup>7)</sup> developed a method that the WF, charge density and band structure are calculated self-consistently. We now extend this description for calculating the energy band of diamond and  $\alpha$ -tin. Owing to the deficiency of the ionic pseudo-potential of  $C^{4+}$  and  $Sn^{4+}$ , it is impossible to get the result in a self-consistent way.

II. METHOD

We are now going to sketch the method for calculating WF for a covalent crystal. By means of a suitable unitary transformation between the WF  $a_m(\vec{r})$  and eigenstates  $\psi_{mk}(\vec{r})$ , Kohn has shown that WF must make stationary the following functional:

$$\epsilon = \sum_{m=1}^M \langle a_m(\vec{r}) | H | a_m(\vec{r}) \rangle \quad (1)$$

Here  $a_m(\vec{r})$  are the WF associated with  $\bar{m}$  connected bands. He also proposed a scheme to obtain the trial WF with a set of localized functions, depending on the variational parameters  $\beta$

$$f_m(\vec{r}) = f_m(\vec{r}, \beta), \quad m = 1, 2, \dots, \bar{m} \quad (2)$$

The function  $f_m(\vec{r})$  are the functions describing the bonding orbitals built up with Slater type orbitals of the valence electrons of atom in a diamond structure, that are given by

$$f_m(\vec{r}) = \frac{1}{\sqrt{2}} \left[ \phi_{\vec{J}_m}(\vec{r}) + \phi_{-\vec{J}_m}(\vec{r} - \frac{1}{4} a \vec{J}_m) \right] \quad (3)$$

and

$$\phi_{\vec{J}_m} = \frac{1}{4} \cdot \frac{1}{\sqrt{\pi}} \left[ F_s(r, \beta_s) + \sqrt{3} \frac{\vec{J}_m \cdot \vec{r}}{r} F_p(r, \beta_p) \right] \quad (4)$$

Here  $a$  is the lattice constant,  $\vec{J}_m$  being the tetrahedral vector in the diamond structure, and  $F_s$  and  $F_p$  are the STO of the valence electron state of the relevant atom

$$F_s(r, \beta_s) = C_s r^{n-1} e^{-\beta_s r} \quad (5)$$

and

$$F_p(r, \beta_p) = C_p r^{n-1} e^{-\beta_p r} \quad (6)$$

Through a Löwdin orthonormalization procedure, a set of trial WF  $a_m^t(\vec{r}, \beta)$  can be built up from a Bloch sum of the function  $f_m(\vec{r}, \beta)$ . This set is specially used to make the functional (1) stationary, and so the variational parameters  $\beta$  are determined giving the actual WF.

The crystal potential consists of an ionic pseudopotential plus the Hartree, exchange and correlation effective potentials produced by the charge in the valence bands. The potential due to the valence charge depends in turn on the variational parameters. Hence, the Hamiltonian is a function of the same parameters and the computation of the stationary value of  $\epsilon$  reduces to the resolution of

$$\sum_{\beta_1} \sum_m \left\langle a_m^{t,v}(\vec{r}, \beta_1) \left| H(\beta_2) \right| a_m^{t,v}(\vec{r}, \beta_1) \right\rangle_{\beta_2 = \beta_1} = 0 \quad (7)$$

the superscript  $v$  in WF indicating that it belongs to valence bands. In actual crystals the spatial integrals make the computation very difficult. The problem can be avoided by writing  $\epsilon$  in the reciprocal space. Once a set of WF is obtained, the valence bands of a covalent crystal can be calculated by diagonalizing the following  $4 \times 4$  matrix

$$\langle \psi_{m\vec{k}}^v(\vec{r}) \left| H \right| \psi_{m\vec{k}}^v(\vec{r}) \rangle \quad (8)$$

in the reciprocal space. For this purpose, we expand the  $\psi_{m\vec{k}}^v(\vec{r})$  as a Fourier series

$$\psi_{m\vec{k}}^v(\vec{r}) = \sum_{\vec{g}} \psi_m(\vec{k} + \vec{g}, \beta) \frac{1}{\sqrt{N\Omega}} e^{i(\vec{k} + \vec{g}) \cdot \vec{r}} \quad (9)$$

The sum of  $\vec{g}$  vector is limited in the region of  $g^2 < 2k \left( \frac{\Omega}{4\pi^2} \right)$ , (i.e. 59  $\vec{g}$  vectors). Finally the actual valence WF can be written as

$$a_m^v(\vec{r}) = \sum_{m'=1}^4 f_{m'}^v(\vec{r} - \vec{n}) \alpha_{m'm}^v(\vec{n}) \quad (10)$$

the coefficient  $\alpha_{m'm}^v(\vec{n})$  determining the spatial dependence of WF. Similarly, we first build up a set of trial localized function  $f_m^c(\vec{r})$  orthogonalizing the valence WF, from a set of non-orthonormal functions  $f_m^c(\vec{r})$ . It can be written as

$$\tilde{f}_m^c(\vec{r}) = f_m^c(\vec{r}) - \sum_{m'=1}^4 \sum_{\vec{n}} a_{m'}^v(\vec{r} - \vec{n}) \gamma_{m'm}(\vec{n}) \quad (11)$$

Here

$$\gamma_{m'm}(\vec{n}) = \langle a_{m'}^v(\vec{r} - \vec{n}) \left| f_m^c(\vec{r}) \right\rangle \quad (12)$$

The conduction WF obviously depends both on the trial function  $f_m^c(\vec{r})$  and the valence WF  $a_m^v(\vec{r})$ . Then diagonalizing the matrix

$$\langle \psi_{m\vec{k}}^c(\vec{r}) | H | \psi_{m\vec{k}}^c(\vec{r}) \rangle \quad (13)$$

One can obtain the eigen-energies of conduction bands of the covalent crystals.

### III. RESULTS AND DISCUSSION

We are going to report the results of silicon, diamond and  $\alpha$ -tin using the method sketched above.

1. One can find out the change of STO parameters going from atom of  $\beta_{s,p}^a$  to the crystal of  $\beta_{s,p}$  as shown in Table I. This is related to the relaxation of electronic wave functions when a solid is formed.
2. Band structure of silicon: We use the ionic pseudopotential of  $Si^{4+}$  given by Schlüter et al.<sup>8)</sup> and compute the band structure in the self-consistent way, the result is shown in Fig.1. The energies at some symmetric points are listed in Table II. These results are in good agreement with those given by others.

In addition, we also compute the same problem using the atomic pseudopotential given by Heine et al.<sup>13)</sup>. In this case it is impossible to make the computation self-consistently, but the results are quite similar to that due to in the self-consistent computation. The difference is in the CB. This result is also shown in Fig.2 and Table II.

3. Band structure of diamond: In this case we use the potential of Saslow et al.<sup>11)</sup> and the computation is non-self-consistent. The result is shown in Fig.3, which is similar to that (Fig.4) given by Hemstreet, Fong and Cohen (HFC)<sup>12)</sup>. One may find out that the energy position order in two figures are similar, but the levels of CB of our result always lie higher than that of HFC. So the main interband transition energy differences of ours are larger than those of theirs (see Table III).

4. Band structure of  $\alpha$ -tin: We use the atomic potential given by Heine et al.<sup>13)</sup> to study the band structure of tin as shown in Fig.5. The result shows that  $\alpha$ -tin is not a picture of semimetal, but it is a semi-

conductor with a gap of 0.2 eV. If we improve the computation in a self-consistent way, it is possible to get a good picture of the  $\alpha$ -tin based on WF.

The above results are quite good to give us some confidence in the method. Hence, we plan to do in the following directions:

1. Making the computation of diamond and  $\alpha$ -tin to be in the self-consistent way.
2. Taking advantage of variational procedure in the ground state of a system, using it to calculate the total energy of Ge, GaAs and ZnSe in the local density functional formalism.
3. Extending the method to study the problems of vacancies and surfaces<sup>15)</sup>.

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TABLE I

STO parameters of the elements and variational parameters of crystals

	Diamond	Silicon	$\alpha$ -tin	
$\beta_s^a$	1.6083	1.6344	0.13	
$\beta_p^a$	1.5679	1.4284	1.82	
$\beta_s$	1.9448	1.6827	1.7305	2.6696
$\beta_p$	1.2468	1.1034	1.1769	1.7391

TABLE II

Band energies in ev at symmetric points of BZ for silicon

	CC*	H**	TV***	present (1)	work (2)
$\Gamma_1$	-12.53	-12.79	-13.17	-13.45	-13.45
$\Gamma_{25}^1$	0	0	0	0	0
$\Gamma_{15}^c$	3.43	2.8	2.61	2.98	2.99
$\Gamma_2^1$	4.17	3.37	2.94	3.32	3.45
$X_1$	-8.27	-8.49	-8.3	-8.45	-8.72
$X_4$	-2.94	-3.16	-3.28	-3.21	-3.55
$X_1^c$	1.22	0.64	1.36	1.83	2.07
$L_2$	-10.17	-10.39	-10.54	-10.99	-10.93
$L_1$	-7.24	-7.57	-7.30	-7.13	-7.71
$L_3$	-1.22	-1.35	-1.50	-1.52	-1.69
$L_1^c$	2.15	1.49	1.65	1.93	2.12
$L_3^c$	4.00	3.63	4.14	5.02	5.38

\* Chelikowsky J.R. and Cohen M.L., Phys.Rev. B14, 556(1976).

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\*\*\* Tejedor C. and Verges J., A. Phys. Rev. B, 19, 2283(1979).

(1) Self consistent

(2) Non self-consistent

TABLE III

The main interband transition energies of diamond (in eV)

	$\Gamma_{25} + \Gamma_{15}$	$\Gamma_{25}' + \Gamma_2$	$L_3' + L_2'$	$L_3' + L_2'$	$X_4 + X_1$	$E_g$
HFC	8.22	6.96	8.27	13.13	11.79	5.46
present	10.40	5.22	8.92	21.45	11.49	4.72

TABLE IV

Eigen energies at some symmetric points of  $\alpha$ -tin (in eV)

$\Gamma_1$	$\Gamma_{25}'$	$\Gamma_{15}^c$	$\Gamma_2'$	$X_1$	$X_4$
-9.898	0	0.213	2.254	-6.695	-2.446
$X_1^c$	$L_2$	$L_1$	$L_3$	$L_1^c$	$L_3^c$
2.989	-8.089	-5.656	-1.203	9.696	4.409

Figure captions:

Fig. 1. Band structure of silicon computed self-consistently in a Wannier function basis.

Fig. 2. Band structure of silicon.

Fig. 3. Band structure of diamond

Fig. 4. Band structure of diamond calculated by Hemstreet, Fong and Cohen.

Fig. 5. Band structure of  $\alpha'$ -tin.

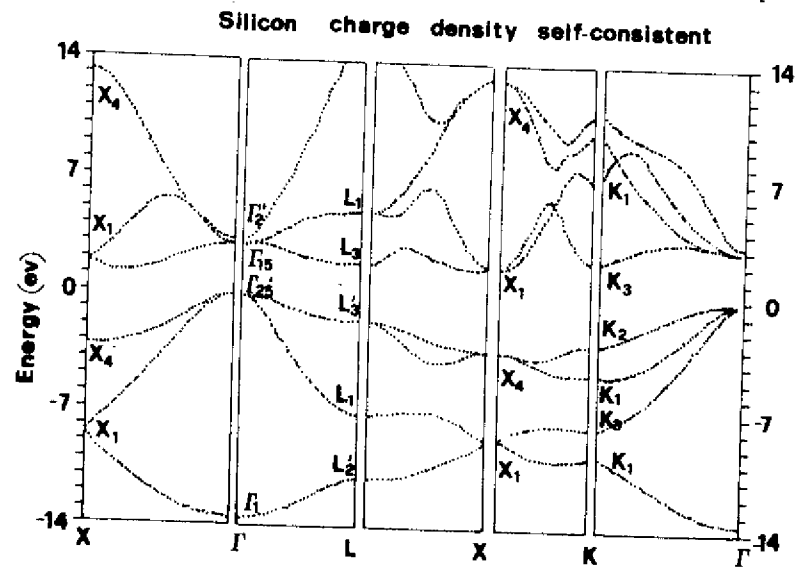


Fig. 1

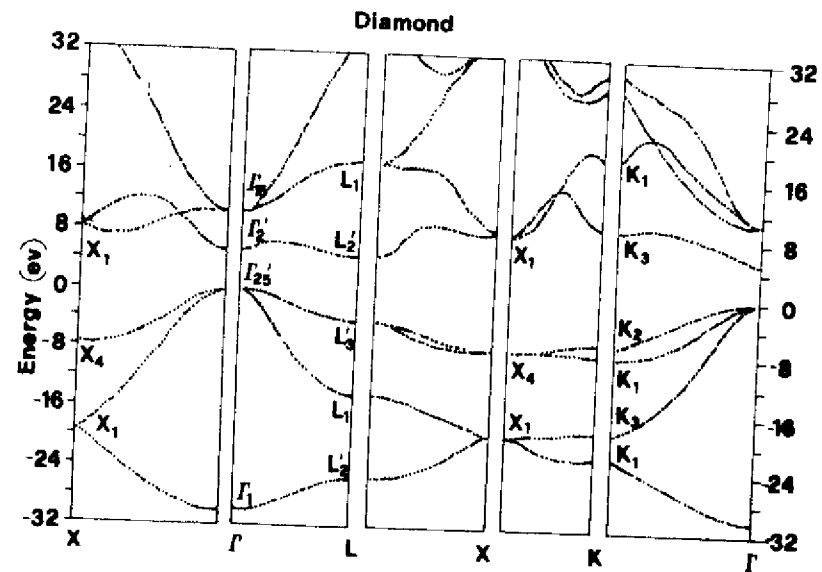


Fig. 3

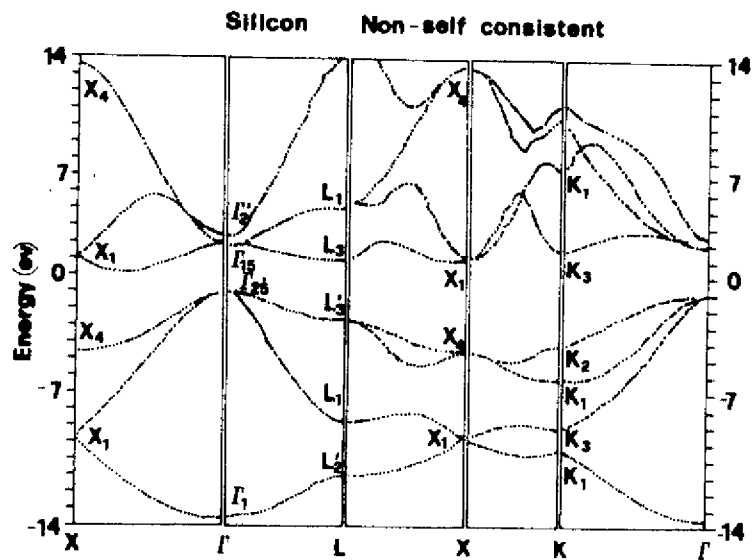


Fig. 2

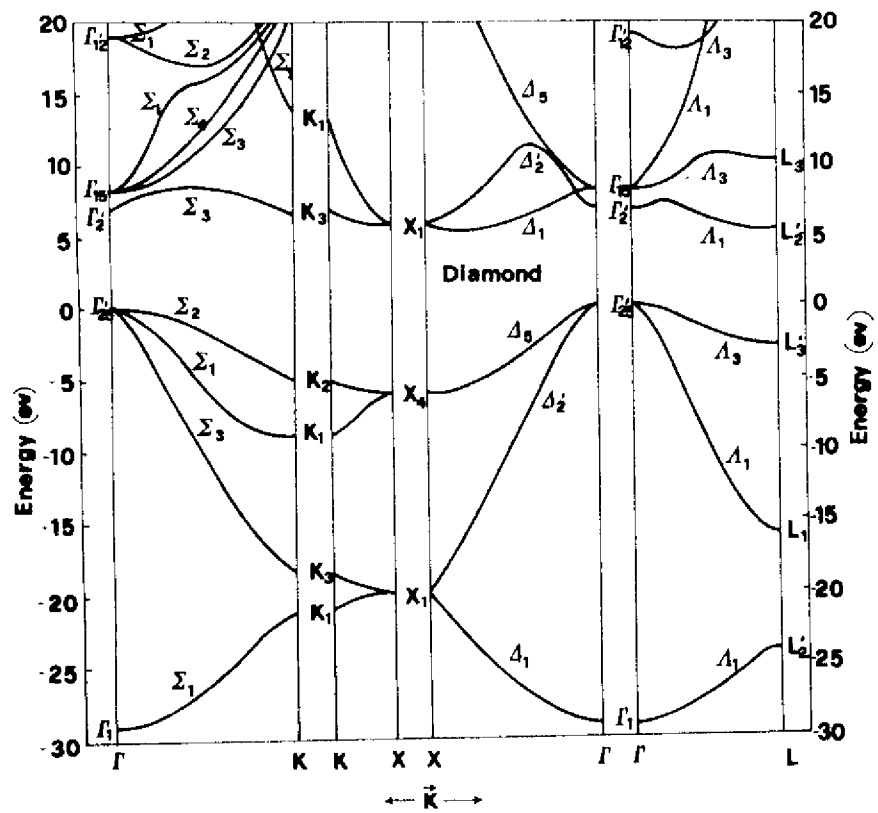


Fig. 4

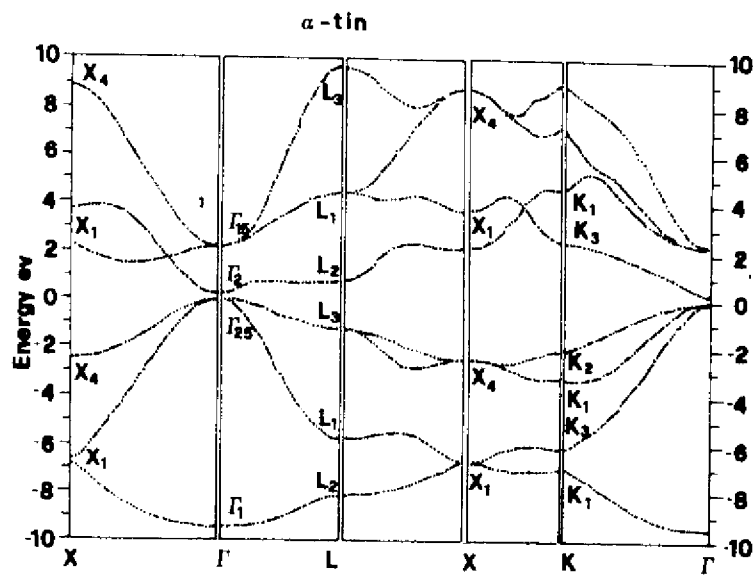


Fig. 5

