Generalized Wannier functions for a model impurity in a one-dimensional lattice

J. P. Albert*

Centre d'Etudes d'Electronique du Solide, Universite des Sciences et Techniques du Languedoc, Montpellier 34060, France

L. Liu

Department of Physics and Astronomy, Northwestern University, Evanston, Illinois 60201

The generalized Wannier function formalism is used to calculate the impurity perturbed electronic structure of a one-dimensional lattice. A comparison is made between this approach and the exact results. It is found that very satisfactory accuracy can be achieved using simple trial functions with only one variational parameter.

I. INTRODUCTION

Since their introduction, the Wannier functions have been proven to be very useful and convenient as an alternate set of functions, equivalent to the Bloch functions, in describing the electronic structure of periodic systems. However, the crystalline periodicity is often interrupted by the presence of an impurity or a surface. To obtain the eigenfunctions in the case of highly localized perturbations, one often uses the well known Slater-Koster theory[1] in which the impurity wave function is expanded in terms of the Wannier functions of the perfect lattice. These form a complete set only if all bands and all lattice sites are taken into account. Yet, as several calculations[2,3] have shown, the convergence in bands may be rather slow and, because of computational limitations, difficult to reach.

Recently, Kohn and Onffroy[4] introduced the generalized Wannier functions (GWF) as an alternate basis for describing the perturbed crystals. These functions are constructed from localized trial functions centered at each lattice site through a variational procedure which minimizes the total energy of the considered band.[5] The principal advantage of using this procedure is that the cumbersome eigenvalue problem can be avoided and the directly obtained GWF are equivalent to the eigenvectors in describing the perturbed system such as its charge density or its density of states. The eigenfunctions may be obtained from these GWF by solving a one-band Slater-Koster-type equation,[4,6] which in this case, is exact.

For a one-dimensional crystal perturbed by a point defect, Kohn and Onffroy[4] have demonstrated that the GWF have exactly the same exponential localization as the perfect Wannier functions and that they approach the latter exponentially for sites distant from the defect. Gay and Smith[7,8] have applied this formalism to a one-dimensional sys-

tem with a surface. They have found that the GWF decay rapidly to the bulk Wannier functions and hence may be constructed with a good accuracy using trial functions which do not depart significantly from their bulk behavior, even in the vicinity of the surface. In this paper we perform a similar test calculation on a model one-dimensional lattice with a perturbation localized in the unit cell. This is to simulate a localized defect in a real crystal. There are many examples of such short-ranged defects: Isoelectronic impurities and vacancies in semiconductors as well as color centers in alkali halides. The calculation of shallow impurity states in semiconductors, taking into account the central cell correction, involves also perturbations strongly varying in the unit cell.[9] It seems therefore of interest to perform such a model calculation in order to gain some guidelines for future work in these problems.

In Sec. II we briefly summarize the GWF formalism in the context of our one-dimensional model. The results of the calculation with an evaluation of their accuracy in comparison with the standard one-band Slater-Koster theory are given in Sec. III. We then give in Sec. IV the main conclusions of our work.

II. APPLICATION OF THE GWF FORMALISM TO A MODEL CALCULATION

In this section we briefly summarize the GWF formalism with special emphasis on its application to a model one-dimensional lattice perturbed by a localized potential.[4] The Hamiltonian of this crystal is given by (unless otherwise specified, atomic units have been used throughout the paper):

$$H = -\frac{d^2}{dx^2} + V_0(x) + v(x), \tag{1}$$

where $V_0(x)$ is the one-dimensional periodic potential and $v(x)$ the localized perturbation.

We shall be only interested in the perturbed states associated with the lowest band. The N perturbed states (where N is the number of cells in the lattice) are given by the solution of the Schrödinger equation

$$H\varphi_j(x) = E_j \varphi_j(x). \tag{2}$$

The GWF formalism is based on the fact that there exists a unitary transformation connecting these states φ_j and a set of localized orthonormal functions a_n so that the ground state of the system may be described equivalently by the following two determinants (assuming noninteracting spinless electrons):

$$\Phi = (N!)^{-1/2} \det |\varphi_j(x_i)|, \tag{3}$$

$$\Phi = (N!)^{-1/2} \det |a_n(x_i)|. \tag{4}$$

The GWF are then constructed from the energy variational principle,[5] based on the fact that the total energy of the perturbed band,

$$E = \sum_{n=1}^{N} \langle a_n(x) | H | a_n(x) \rangle, \tag{5}$$

attains its minimum value when the a_n form the correct set of GWF. This minimization procedure must be carried out with trial functions a_n^t which are orthogonal. They are constructed from localized atomiclike functions $g_n(x)$ centered at each lattice site which are orthogonalized by the symmetric orthogonalization procedure of Lowdin[10]:

$$a_n^t(x) = \sum_l S_{nl}^{-1/2} g_l(x), \tag{6}$$

where S is the overlap matrix

$$S_{nl} = \langle g_n(x) | g_l(x) \rangle. \tag{7}$$

In our test calculation $V_0(x)$ has been chosen to be a Mathieu potential

$$V_0(x) = \sigma^2 d^2 [1 - \cos(2\pi x/d)], \tag{8}$$

where the parametrization of Gay and Smith[7] has been adopted:

$$d = lt, \tag{9}$$
$$\sigma^2 = \tfrac{1}{2}\pi^2(1/t^4).$$

Here d is the lattice constant, l a parameter governing the strength of the potential, and t a scaling parameter introduced in order to produce realistic values for energies and lengths. We then superimpose to this potential a perturbation given by

$$v(x) = \lambda\sigma^2 d^2[1 + \cos(2\pi x/d)], \quad |x| \leq \tfrac{1}{2}d,$$
$$v(x) = 0, \quad |x| > \tfrac{1}{2}d, \tag{10}$$

where λ may be varied in order to produce · different depths for the perturbed well at the

origin. Positive values of λ produce repulsive perturbations which pull out a state from the top of the considered band while negative values result in a state split off from the band bottom. The connection between these model Mathieu potentials and real crystals has been extensively discussed by Slater.[11] The potential minima are the atomic sites and the appropriate "atomic orbitals," i.e., the approximate solutions of the Mathieu equation in the vicinity of the minimum, are the harmonic oscillator wave functions. These offer thus a simple and natural choice for the set of trial functions g_l. As we are only interested in the lowest band, these trial functions are the simple "s" Gaussians:

$$g_l(x) = (\sqrt{\alpha_l}/\pi^{1/4}) \exp[-\tfrac{1}{2}\alpha_l^2(x - l)^2], \tag{11}$$

where α_l are the variational parameters.

III. CALCULATIONS AND RESULTS

The test calculations are carried out for two different choices of parameters for the Mathieu potential. We shall label them as the W abd S potentials after Gay and Smith.[7] The chosen parameters are: $l = 1$, $t = 5$ for the W potential and $l = 2^{1/4}$, $t = 5$ for the S potential. These values give rise to a nearly free-electron character for the lowest band. The interaction between the wells is stronger with the W potential and results in a wider band than in the case of the S potential. We shall first assign the values of -0.4 and $+0.4$ for the perturbation parameter λ in association with the W and S potentials, respectively. These model potentials are shown in Figs. 1 and 2.

We first consider the unperturbed lattice and construct its Wannier function a_n^0. Because of the periodicity, all the sites and thus all the g_l are
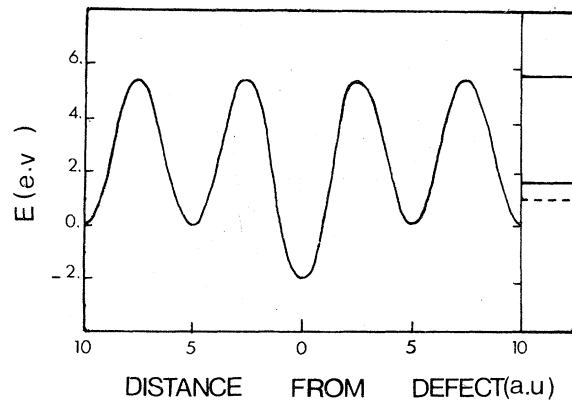

FIG. 1. Illustration of the "W" model impurity potential with $\lambda = -0.4$. The band edges (solid lines) and impurity state (dotted line) are shown on the right of the figure.
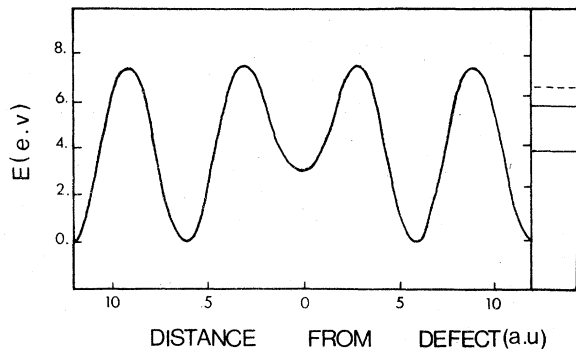
FIG. 2. Illustration of the "S" model impurity potential with $\lambda = +0.4$. The band edges (solid lines) and impurity state (dotted line) are shown on the right of the figure.

equivalent. The variational calculation involves thus only one parameter, i.e., the width of the identical trial Gaussian functions. Once the Wannier functions of the perfect lattice are obtained from these "optimized" g_i^0, we construct the GWF of the perturbed crystal, allowing the widths of the Gaussians to depart from their unperturbed value. As the GWF are expected to approach the unperturbed Wannier functions for sites distant from the perturbation, it is only necessary to vary the widths of the Gaussians centered in the vicinity of the defect site. In fact we found that only the central cell Gaussian needs to be varied, the others keeping their original value. Hence, the damping of the GWF to the unperturbed Wannier functions is very rapid and is completed by the third site for the W potential ($\lambda = -0.4$) and the second for the S model potential ($\lambda = +0.4$). We plot in Fig. 3 an example of GWF which is compared with the unperturbed Wannier function. We have also chosen several other values for the parameter λ and in each case found that only the central cell Gaussian needs to be varied. The optimized values for the widths of the central cell Gaussian are given in Table I. We have also augmented the variational scope of our trial functions by taking a linear combination of "s" and "p" Gaussians for the g_i centered at the first neighbors of the defect. (Because of the inversion symmetry there is no p component on the site of the defect.) However, we found that this does not lower the energy minimum and that these functions had to keep their unperturbed value. The fact that only the central cell Gaussian is affected by even a strong perturbation is very encouraging for extending the present calculation to more realistic systems. In particular, extending this work to three-dimensional crystals may be computationally feasible if only the defect centered trial function
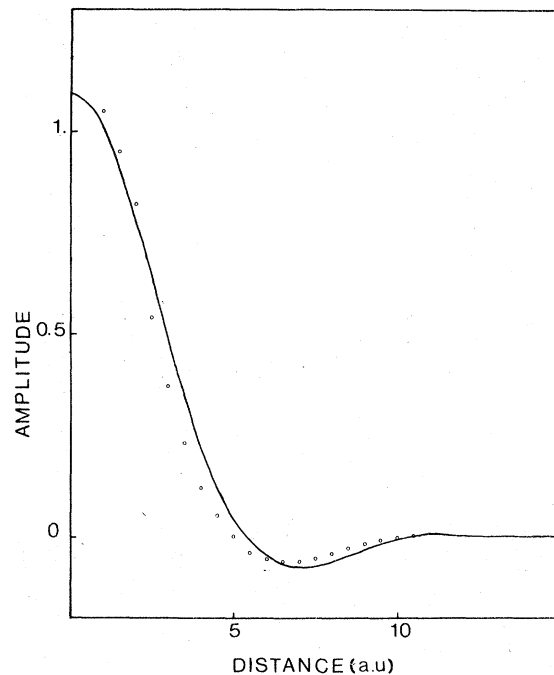

FIG. 3. Illustration of the central site GWF for the "S" model potential with $\lambda = +0.4$. This GWF is compared with the unperturbed Wannier function (open circles).

has to be varied. The rapid decay of the GWF to the unperturbed behavior may be seen by comparing the matrix elements $\langle a_i | H | a_i \rangle$ with the ones obtained using the unperturbed Wannier functions. These comparisons are made in Tables II and III for two extreme cases. From these tables, it appears that by the third site the GWF have regained their unperturbed behavior.

In order to study the accuracy of our calculations, we have calculated the energy and the wave function of the impurity states and compare them to the exact results obtained by numerically integrating the Schrödinger equation. In the GWF

TABLE I. This table gives for the W and S potentials the widths of the central cell Gaussian for different values of the perturbation parameter λ. The other Gaussians keep their corresponding unperturbed width ($\lambda = 0$).

λ	W potential $\alpha_0 d/\pi$	S potential $\alpha_0 d/\pi$
+0.6	0.47	0.53
+0.4	0.54	0.64
+0.2	0.62	0.72
0	0.69	0.78
−0.2	0.75	0.84
−0.4	0.80	0.89
−0.6	0.85	0.94

TABLE II. Matrix elements of the Hamiltonian between GWF (second column) and unperturbed Wannier functions (third column). The first column gives the number of the considered site (see Fig. 1). This is the case studied where the damping of the GWF to the unperturbed Wannier functions is the least rapid. (W potential, $\lambda = +0.6$). Results are in electron volts.

n	$\langle a_n|H|a_n\rangle$	$\langle a_n^0|H|a_n^0\rangle$
0	5.6289	6.0834
1	4.4134	4.2470
2	4.2300	4.2237
3	4.2235	4.2227
4	4.2228	4.2227
5	4.2227	4.2227

formalism, the perturbed band states can be obtained by solving a one-band-type Slater-Koster equation.[6] However, it is much simpler in our case to obtain these directly by solving the Schrödinger equation (2) for a cluster of atoms surrounding the defect. We expand the eigenfunctions in terms of the GWF:

$$\varphi_j = \sum_n C_{nj} a_n \qquad (12)$$

and rewrite Eq. (2) as a matrix equation in terms of the expansion coefficients C:

$$\sum_{n'} \langle a_n|H|a_{n'}\rangle C_{n'j} = E_j C_{nj} . \qquad (13)$$

We have found that taking a cluster of 40 sites is more than sufficient to produce converging results. The impurity wave functions so obtained are plotted in Fig. 4 for the W potential with $\lambda = -0.4$ and Fig. 5 for the S potential with $\lambda = +0.4$. We also give in Figs. 4 and 5 the results obtained by expanding the impurity wave function in terms of the unperturbed Wannier functions (one-band Slater-Koster theory). From Figs. 4 and 5 one can see that even with simple trial functions, we

TABLE III. Matrix elements of the Hamiltonian between GWF (second column) and unperturbed Wannier functions (third column). The first column gives the number of the considered site (see Fig. 2). This is the case studied where the damping of the GWF to the unperturbed Wannier functions is the most rapid (S potential, $\lambda = -0.2$). Results are in electron volts.

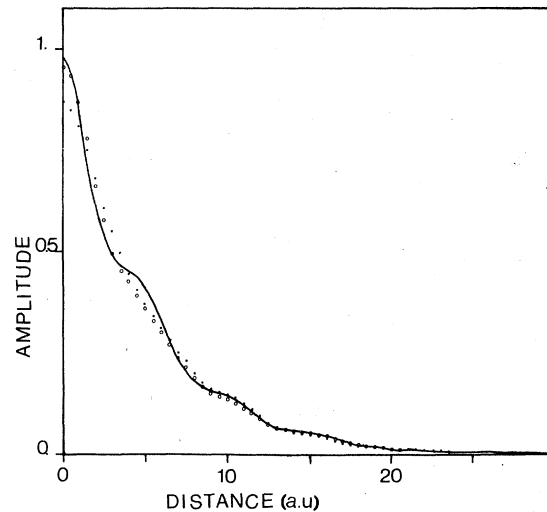| n	$\langle a_n|H|a_n\rangle$	$\langle a_n^0|H|a_n^0\rangle$
0	3.3708	3.3743
1	4.3659	4.3785
2	4.3783	4.3785
3	4.3785	4.3785

FIG. 4. Impurity state wave function for the W model potential with $\lambda = -0.4$. The exact wave function (solid line) is compared with the ones obtained with the GWF formalism (open circles) and the Slater-Koster one-band theory (solid points). The corresponding energies are, respectively, 2.020, 2.077, and 2.170 eV.

can obtain reasonable accuracy and that the GWF formalism improves the standard Slater-Koster results.

IV. CONCLUSION

In this study, we have calculated the GWF of a one-dimensional crystal pertrubed by an impurity localized in the unit cell. These GWF are found
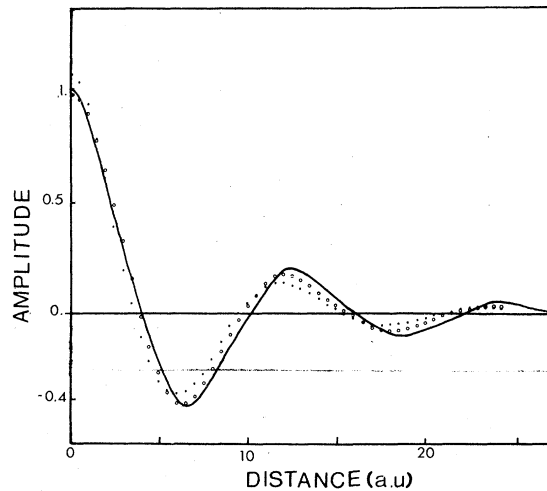

FIG. 5. Impurity state wave function for the S model potential with $\lambda = +0.4$. The exact wave function (solid line) is compared with the ones obtained with the GWF formalism (open circles) and the Slater-Koster one-band theory (solid points). The corresponding energies are, respectively, 6.577, 6.661, and 6.778 eV.

to decay rapidly to the unperturbed Wannier functions when one goes away from the defect site. We have shown that, even for fairly strong perturbations, the construction of these GWF involves only the optimization of the atomiclike trial function centered on the defect. We have also shown that the use of the GWF formalism can improve the calculated energy and wave function of the impurity state over the one-band Slater-Koster solutions. All these results are very encouraging for extending this type of calculations to three-dimensional crystals. For example, the calculation of deep impurity states in semiconductors has to be done self-consistently in order to take into account the polarization of the host lattice by the defect. The GWF formalism is especially well suited for this purpose because these functions give directly the charge rearrangement near the defect. Owing to the accuracy achieved here with simple trial functions and only one variational parameter, it is felt that such calculations may be computationally feasible for a realistic system.

*Visitor to Dept. of Physics and Astronomy, Northwestern University under a NATO Fellowship.

[1] G. F. Koster and J. C. Slater, Phys. Rev. 95, 1167 (1954).

[2] R. A. Faulkner, Phys. Rev. 175, 991 (1968); J. Callaway and A. J. Hughes, *ibid.* 156, 860 (1967); N. Parada, *ibid.* B 3, 2042 (1971).

[3] E. Ducla-Soares and R. L. Lozes, J. Phys. C 10, 4965 (1977).

[4] W. Kohn and J. Onffroy, Phys. Rev. B 8, 2485 (1973).

[5] W Kohn, Phys. Rev. B 1, 4388 (1973).

[6] J. G. Gay and J. R. Smith, Phys. Rev. B 9, 4151 (1974).

[7] J. G. Gay and J. R. Smith, Phys. Rev. B 11, 4906 (1975).

[8] J. R. Smith and J. G. Gay, Phys. Rev. Lett. 32, 774 (1974).

[9] J. R. Onffroy, Phys. Rev. B 17, 2062 (1978).

[10] P. O. Löwdin, J. Chem. Phys. 18, 365 (1950).

[11] J. C. Slater, Phys. Rev. 87, 807 (1952).