

SELF-CONSISTENT PSEUDOPOTENTIALS
AND ULTRALOCALIZED FUNCTIONS FOR ENERGY BANDS

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(Received 13 May 1968)

We present a pseudopotential method for calculating very localized functions representing energy bands in molecules and solids.

An isolated energy band in a periodic potential may be represented by localized, orthogonal Wannier functions

$$W_n(r) = \sum_k \exp(ik \cdot R_n) b_k(r), \quad (1)$$

where b_k is the Bloch function. Blount¹ summarizes the problem of how to choose the phases of the b_k in order to best localize W , and Kohn² and Blount¹ have given theorems showing that the asymptotic behavior of $W_n(r)$ at large r is controlled by $\exp(-k_b |r|)$ where k_b is a branch point in complex k space, of the order of the smallest band gap involving the given band.

It is trivial to show that W is not the best-localized linear combination of all Bloch functions. It has long been guessed, in molecular theory at least,³ that essentially equivalent nonorthogonal functions are better localized. Formally, write a normalized nonorthogonal function

$$\varphi_0(r) = \frac{W_0(r-R_0) + \sum_{n \neq 0} S(n) W_n(r-R_n)}{[1 + \sum_n |S(n)|^2]^{1/2}} \quad (2)$$

and find the mean squared radius $\langle r^2 \rangle$ of φ_0 compared with that of $W (= \langle r_0^2 \rangle)$:

$$\begin{aligned} \int \varphi_0^2(r) (r-R_0)^2 d^3r = & \langle r_0^2 \rangle + \sum_{n \neq 0} S_n^2 \int [(r-R_n) + (R_n - R_0)]^2 W_n^2 d^3r \\ & + 2 \sum_{n \neq 0} S_n \int W_n W_0 \left[r - \left(\frac{R_0 + R_n}{2} \right) - \left(\frac{R_0 - R_n}{2} \right) \right]^2 d^3r \\ & + 2 \sum_{n, n' \neq 0} S_n S_{n'} \int W_n W_{n'} (r-R_0)^2 d^3r \left(1 + \sum_n S_n^2 \right)^{-1}. \end{aligned}$$

Using

$$\int W_n W_{n'} \left[r - \frac{1}{2}(R_n + R_{n'}) \right]^2 d^3r = 0 \quad (3)$$

and orthonormality of W , we get

$$\begin{aligned} \langle (r-R_0)^2 \rangle = \langle r_0^2 \rangle + & \left\{ \sum_n S_n^2 (R_n - R_0)^2 + 2 \sum_n S_n \int W_n W_0 \left(r - \frac{R_0 + R_n}{2} \right)^2 d^3r \right. \\ & \left. + 2 \sum_{n, n' \neq 0} S_n S_{n'} \int W_n W_{n'} \left(r - \frac{R_n + R_{n'}}{2} \right)^2 d^3r \right\} \left(1 + \sum_n S_n^2 \right)^{-1}. \end{aligned} \quad (4)$$

Clearly, since this contains terms linear in S_n it can be decreased by introducing a finite S_n of the order of

$$S_n \approx - \frac{\int W_n W_0 \left[r - \frac{1}{2}(R_0 + R_n) \right]^2 d^3r}{(R_n - R_0)^2}, \quad (5)$$

and all other terms are of higher order in S_n .

The numerator of (5) is manifestly nonzero; if the W are orthogonal, $W_n W_0$ must be even and negative near the atoms n and 0 , positive between, so in fact S_n should be positive (for an s band). This is in the direction of making the Wannier functions more like atomic orbitals. Thus a great deal of the annoying nonlocality of

Wannier functions is an inessential consequence of orthogonalization. This is however not true of the exponential tail, we believe (for reasons shortly to be discussed); however, the exponentials result only from branch points and may turn out to be rather small quantitatively.

Next we show that there is a general pseudopotential formalism giving a wave equation which such localized functions satisfy, and that the pseudopotential may be chosen to give functions more localized than Wannier functions.

First, consider the Wannier equation⁴ as a possible pseudopotential equation to be solved for $W(r-R_n)$:

$$\mathcal{H}_{\text{ps}}^n W = EW, \quad (6)$$

$$\mathcal{H}_{\text{ps}}^n f(r) = \mathcal{H}f(r) - \sum_{n' \neq n} \langle n' | \mathcal{H} | f(r) \rangle W_n'(r).$$

We could try to solve this equation by iteration, starting with a localized approximation to $W(r)$ and inserting that on the right-hand side for all $W_{n' \neq n}$. The resulting Wannier function could then be reinserted, etc.

Unfortunately, this procedure may be at best

$$\mathcal{H}\psi_k = E\psi_k + \sum_{n, n' \neq n} \exp(ik \cdot R_n) \langle \varphi_n | \mathcal{H}^{\text{out}} | \varphi_n \rangle \varphi_n(r), \quad (8)$$

$$= E\psi_k + \sum_{n-n'} \exp[ik \cdot (R_n - R_{n'})] \langle \varphi_n | \mathcal{H}^{\text{out}} | \varphi_n \rangle \psi_k \quad (9)$$

so that ψ_k is a valid Bloch-wave solution of

$$\mathcal{H}\psi_k = E_k \psi_k. \quad (10)$$

Note that E_k is given by (9): The matrix elements $\langle n' | \mathcal{H}^{\text{out}} | n \rangle$ must be identical with the actual Wannier-function matrix elements $\langle n' | \mathcal{H} | n \rangle$, and the energy expression does not contain overlap matrix elements even though the wave functions are nonorthogonal. This is possible because the pseudo-Hamiltonian is non-Hermitian. If the wave functions are more localized than Wannier functions (and we shall see that \mathcal{H}^{out} may be chosen more local, too), this shows that some of the Wannier-function nonlocality is irrelevant to the energy matrix. This is why the branch points must, however, appear: They are a property of the energy matrix, not the wave functions.

I have no method of choosing a best \mathcal{H}^{out} but certainly a good one is as follows. Let us suppose that (as is usually a very good approxima-

tion for energy-band problems)

tion for energy-band problems) slowly convergent and at worst unstable. Even the most localized Wannier functions usually have large negative amplitudes at atom n' , which have to be generated by the self-consistency procedure. In the process, we are in danger of losing all localization, since the Bloch functions satisfy the pseudopotential equation (for them all off-diagonal elements of \mathcal{H} are just zero).

We observe that we have actually an enormous freedom of choice in the pseudopotential term. Instead of \mathcal{H} we may insert any operator \mathcal{H}^{out} which has the property that its matrix elements between functions centered at R_n and $R_{n'}$ are functions of $R_n - R_{n'}$ alone. We demonstrate that this is the case: Let $\varphi_n(r)$ be a localized function satisfying the pseudopotential equation

$$E\varphi_n(r) = \mathcal{H}^n \varphi_n(r) = \mathcal{H}\varphi_n(r) - \sum_{n' \neq n} \langle n' | \mathcal{H}^{\text{out}} | n \rangle \varphi_n'(r).$$

Let us now make up a Bloch wave from the (now nonorthogonal, but linearly independent) functions φ_n :

$$\psi_k = \sum_n \exp(ik \cdot R_n) \varphi_n, \quad (8)$$

tion for energy-band problems)

$$\mathcal{H} = T + \sum_n V(r - R_n), \quad (11)$$

where the V 's may overlap somewhat if desired. Let me then choose

$$\mathcal{H}_{\text{ps}}^n = T + V_n + \sum_{n' \neq n} V_{n'} \times [\delta(r - r') - \varphi_n(r) \varphi_n'(r')], \quad (12)$$

where the nonlocal term is meant in the sense

$$\mathcal{H}_{\text{ps}}^n \varphi_n(r) = (T + V_n) \varphi_n(r) + \sum_{n' \neq n} [V_{n'}(r) \varphi_n(r) - (\int \varphi_n \cdot V_{n'} \varphi_n) \varphi_n(r)]. \quad (13)$$

As has been frequently discussed in the literature dealing with the pseudopotential method,⁵ the effect of the subtracted term is to remove from V_n a large fraction of its ability to bind, i.e., to change V from a strong to a weak potential. Thus φ_n can probably in many cases simply be taken as approximately an eigenfunction of $T+V_n$, and the effect of the pseudopotential is weak and can be treated by low-order perturbation theory. If so, self-consistency is easily achieved. It is a fascinating fact that the effect of the pseudopotential terms on the eigenvalue E can be quite large (their diagonal matrix elements are relatively large because the overlap S_{nm} may be quite large), but as perturbations on the wave function φ_n they are relatively ineffective. The diagonal matrix element is what is responsible for the overlap repulsion between closed shells.

To show that our new functions are nonorthogonal, multiply the pseudopotential equation on the left by φ_m and integrate:

$$E(\varphi_m | \varphi_n) = (\varphi_m | \mathcal{H} | \varphi_n) - \sum_n (\varphi_n | \mathcal{H}^{\text{out}} | \varphi_n) (\varphi_m | \varphi_n) + (\varphi_n | \mathcal{H}^{\text{out}} | \varphi_n) (\varphi_m | \varphi_n),$$

i.e., $(E - \langle H^{\text{out}} \rangle) \mathbf{S} + H^{\text{out}} \mathbf{S} = H$, where \mathbf{S} is the overlap matrix:

$$\mathbf{S} = \mathbf{H} [E - \langle H^{\text{out}} \rangle + H^{\text{out}}]^{-1}.$$

Only when $H^{\text{out}} = H$ is this the unit matrix. When $\langle H^{\text{out}} \rangle \approx 0$ and H^{out} is itself effectively (not actually) small, we have $\mathbf{S} \approx \mathbf{H}/E$, a relation which is often used in reverse for approximate molecular calculations. Thus this is a criterion for good wave functions, not a consequence of evaluating linear combination of atomic orbital integrals.

Possible applications of this formalism to solid-state physics and quantum chemistry are manifold. In solid-state physics, ionic and other closed-shell crystals are an obvious example; also the surprising success of the tight-binding method without overlap for d bands⁶ (or at least for the d -band submatrix of the secular equation) may be cited. In covalently bonded molecules and solids, it may be necessary to use hybridized bond functions for φ_n and modify \mathcal{H}^{out} accordingly. A paper on the application of the

method to the foundations of the Hückel theory of π electrons in aromatic molecules⁷ is in preparation. It can be shown that periodicity is not at all essential; what is needed is basically a well-separated band of energy states.

It is possible, we feel, that in many of these cases the accurate solution of the one-electron problem can be reduced to perturbation theory by the self-consistent pseudopotential method.

After the completion of this work my attention was drawn to the sequence of papers by Adams, Gilbert, and Edmiston and Rudenberg referred to in Ref. 3. By taking advantage of the arbitrariness in the diagonalization of the Hartree-Fock (H-F) equations, these authors have introduced a self-consistent pseudopotential into these equations. They show that this leads to localized functions which, by actual construction in some small-molecule cases for which exact H-F solutions were known, are well localized. They also point out the possibility of application to large chemical systems: of "making molecules out of building blocks" (Gilbert), and of determining the functions via the pseudoequation itself (Edmiston and Rudenberg); and Adams observes that this gives Löwdin's work on the alkali halides a sounder justification than heretofore. Nonetheless, this ambitious program has not been realized, because, I believe, of weaknesses in their formalism as well as a lack of emphasis on this goal. Some formal problems are these: (1) The connection with H-F, which is not necessary, allows rediagonalization only among the occupied levels. By the theorems on Wannier functions, this prevents any meaningful localization except for full bands: closed shells or saturated covalent bonds. In particular, d bands and the Hückel theory are excluded. Also, the neat and simple form of the secular equation loses its meaning, as well as the connection back to the Wannier equation which is relevant for the many-electron problem. (2) The use of the density matrix as a projector, which is bound up with the unnecessary and awkward requirement of a Hermitian pseudo-Hamiltonian (it is interesting that Hermitian pseudo-Hamiltonians are awkward also in the very different conventional pseudopotential theory), introduces a nonlocality (because of the presence of the overlap matrix in the definition of ρ) which is as severe as that in the Wannier functions. The pseudopotential is then not confined to the peripheral regions, which blocks the straightforward use of perturbation theory.

In spite of these objections, I feel these papers have made a contribution the great importance of which should be more widely recognized.

I would like to acknowledge stimulating and useful discussions with E. I. Blount, R. G. Shulman, and M. H. Cohen.

¹E. I. Blount, in *Advances in Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1962), Vol. 13, p. 305, especially Chap. III and Appendix C.

²W. Kohn, *Phys. Rev.* **115**, 809 (1959).

³This is assumed, and proven for small molecules, in the sequence of papers using similar methods which

I will discuss at the end of this paper: W. H. Adams, *J. Chem. Phys.* **34**, 89 (1961), and **37**, 2009 (1962); C. Edmiston and K. Rudenberg, *Rev. Mod. Phys.* **35**, 457 (1963); T. L. Gilbert, in *Molecular Orbitals, a Tribute to R. S. Mulliken*, edited by P. O. Löwdin and B. Pullman (Academic Press, Inc., New York, 1964), p. 405. But one may find the contrary statement: see R. McWeeny, in *Molecular Orbitals, a Tribute to R. S. Mulliken*, edited by P. O. Löwdin and B. Pullman (Academic Press, Inc., New York, 1964), p. 311.

⁴G. F. Koster, *Phys. Rev.* **89**, 67 (1953).

⁵B. J. Austin, V. Heine, and L. J. Sham, *Phys. Rev.* **127**, 276 (1962) (for a summary of the pseudopotential point of view).

⁶F. M. Mueller, *Phys. Rev.* **153**, 659 (1967).

⁷C. A. Coulson, *Valence* (Oxford University Press, New York, 1961), Chap. IX.

SOFT PHONON MODES AND THE 110°K PHASE TRANSITION IN SrTiO₃

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(Received 20 May 1968)

We propose a new interpretation of the 110°K phase transition in SrTiO₃, in which the essential feature is a soft phonon at the corner of the cubic Brillouin zone. This interpretation is supported by new evidence from the temperature-dependent Raman spectrum as well as by results of earlier experiments and calculations. Several other experimental results are explained or predicted on the basis of our model for the phase transition.

Strontium titanate is known to undergo a non-ferroelectric phase transition at $T_0 = 110^\circ\text{K}$ from a cubic perovskite to a tetragonal structure.^{1,2} Yet the detailed nature of the phase transition has remained unclear. Associated with the phase transition are striking changes in the sound velocity,³⁻⁵ the Rayleigh⁴ and Raman^{5,6} spectra, and the ESR.^{2,7} In this Letter we propose a microscopic model for the 110°K phase transition which provides a basis for understanding the above experiments³⁻⁷ and which is supported by new evidence from the temperature-dependent Raman spectrum. Our interpretation is motivated largely by the low-temperature structure (D_{4h}^{18}) of SrTiO₃, suggested in the recent ESR work by Unoki and Sakudo,⁷ and is fundamentally different from the interpretation of Cowley.⁸ The basic features of our model are (a) that as $T \rightarrow T_0$ from above, the triply degenerate phonon F_{2u} (Γ_{25}) at the R point of the Brillouin zone softens (approaches zero frequency); (b) for $T \leq T_0$ the point R is then a reciprocal lattice point so that the unit cell is twice as large as in the cubic phase and the number of zone-center excitations is doubled; (c) as T is lowered from T_0 , the two new zone-center phonons, whose progenitor was

the F_{2u} zone-corner phonon, increase in frequency or "harden."

Our experimental evidence for these conclusions consists of (1) the appearance of several sharp lines in the Raman spectrum below 110°K, (2) a definite softening of two of these phonon frequencies as $T \rightarrow T_0$ from below (see Fig. 1), and (3) the direct interaction of these two phonons with components of the "ferroelectric" mode, observed using the technique of electric-field-induced Raman scattering⁹ (EFIRS) and by tuning the "ferroelectric" mode frequencies with an electric field.¹⁰

The experimental apparatus is as described elsewhere.^{10,11} The intrinsic (no external electric field) Raman spectra for various temperatures have been presented elsewhere and need not be reproduced here.^{6,11-14} Above 110°K the spectrum consists of several broad bands which have been interpreted, we believe correctly, by Nilsen and Skinner⁶ as entirely due to second-order scattering. Below 110°K five additional sharp lines appear at 15, 48, 146, 235, and 460 cm^{-1} . (These are the frequencies at 15°K.) While most of the features have been noticed by other workers,^{6,12-14} they have always been, in