Electronic States in Complicated Materials: The Recursion Method [and Discussion]

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Electronic states in complicated materials: the recursion method

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The determination of electronic states in complicated materials is difficult because of large numbers of inequivalent and nearly degenerate electronic orbitals. The only available approach is direct integration of the Schrödinger equation by path summation for which the recursion method gives a convergent expansion of the energy resolvent as a continued fraction whose parameters may be expressed as summations of groups of mutually avoiding paths. The inverse Fourier transforms of these continued fractions are matrix elements of the propagator and hence provide convergent discrete approximants for Feynman path integrals. Path counting for sequences of close packed layers is illustrated, and the application of the recursion method to the structural stability of transition metal Laves phases is reviewed briefly.

1. Introduction

The calculation of electronic states for materials with large numbers of inequivalent atoms requires a general solution of the Schrödinger equation. In such complicated materials, the coupling between electronic orbitals is usually larger than the differences in the energies of the orbitals so that perturbation theory for the electronic states does not converge, and because there are so many orbitals, a variational approach requires minimization with respect to a large number of parameters. In such circumstances the only approach is direct integration which, because the systems are two or three dimensional, requires path summation or path integration.

This paper describes the recursion method (Haydock 1980), a general solution to the Schrödinger equation, which has been used for the past 20 years to calculate densities of states and other electronic properties of materials with defects, disorder, or large unit cells. The idea behind this method is that instead of trying to calculate all the electronic states of the system, only those accessible from a given initial orbital are determined. The electronic hamiltonian is recursively transformed into a tridiagonal matrix by constructing a set of basis orbitals, of which the first is the initial orbital. This process of tridiagonalization can be viewed in a variety or ways: as direct integration of the Schrödinger equation in the non-degenerate subspace of states accessible from the initial orbital, as a variational solution of the Schrödinger equation in the subspaces spanned by powers of the electronic hamiltonian on the initial orbital, or even as a method for summing infinite sets of terms in perturbation theory.

This work returns to the origin of the recursion method in the counting of quantum mechanical paths and presents a way of expressing physical quantities in terms of a

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set of elementary determinants of paths. Friedel (1954) pointed out that the moments, integrals over powers of energy, of the density of states projected on an orbital, are the sums of products of the matrix elements of the hamiltonian along the paths which begin and end at that orbital. This idea was applied by Cyrot-Lackmann (1970) to the local densities of states of transition metals, and by Burdett (1986) to a variety of solid structures. Because the moment expansion of physical quantities does not converge Haydock *et al.* (1972*a*) developed the recursion method as a direct relation between the hamiltonian and the density of states. One objection to the recursion method has been that the intuitive appeal of path counting was lost and that the matrix elements of the hamiltonian in tridiagonal form have no simple physical interpretation. It is shown below that instead of these matrix elements, physical quantities can be expressed in terms of sums of mutually avoiding quantum mechanical paths. Some simple examples of chemical reactivity and structural stability are used to illustrate the ideas of path counting, and the application of the recursion method to the structural stability of the transition metal Laves phases is briefly reviewed.

The time development of a quantum mechanical system is given by the propagator, $\exp\{-\mathrm{i}\boldsymbol{H}t\}$, applied to the initial state of the system ϕ_0, where $\boldsymbol{H}$ is the hamiltonian and t is time. However, for the purposes of this work, it is more convenient to work with the Fourier transform of the propagator which is the energy resolvent $1/(E-\boldsymbol{H})$. The result of multiplying ϕ_0 by the resolvent is singular on the invariant states of $\boldsymbol{H}$, contained in ϕ_0, with energy E. The time-dependent evolution of ϕ_0 can be recovered by an inverse Fourier transform, and similarly, time-dependent expressions can be recovered from all that follows.

2. Quantum path counting

Although either the full propagator or the full resolvent can be expanded in terms of quantum path summations, in the interests of simplicity, consider just the diagonal element of the resolvent,

$$R(E) = \phi_0^*(E-\boldsymbol{H})^{-1}\phi_0, \tag{2.1}$$

where in Dirac's notation ϕ_0^* is the bra corresponding to the ket ϕ_0. Physically this describes the energy spectrum of the invariant states contained in ϕ_0, and its Fourier transform is the propagator element for the system to start in ϕ_0 and return to it after a time t.

Expansion of this resolvent element in paths in equivalent to expansion of the resolvent in powers of the hamiltonian,

$$R(E) = \Sigma\,\phi_0^*\,\boldsymbol{H}^n\phi_0(1/E)^{n+1}, \tag{2.2}$$

where the sum is over n from nought to infinity. The expectation value $\phi_0^*\boldsymbol{H}^n\phi_0$ is converted to a path summation by introducing a countable, complete set of basis orbitals $\{\phi_m\}$ to make,

$$R(E) = \Sigma\,\mu_n/E^{n+1}, \tag{2.3}$$

with

$$\mu_n = \Sigma\,H_{0,1}H_{1,2}\ldots H_{n-1,0}, \tag{2.4}$$

where the sum is over all paths of n steps beginning with ϕ_0, going from one basis orbital to another, and ending with ϕ_0; and each term in the sum is the product of the matrix elements of $\boldsymbol{H}$ for each step of that path. The expansion in quantum paths is always possible because there is always a countable complete set of orbitals, for example the isotropic oscillator wavefunctions, or the orbitals localized within each atomic cell. Since each path has a finite number of steps, the product of the matrix elements of the hamiltonian is finite for each path; however, the expansion of the resolvent in inverse powers of E, and the corresponding expansion of the propagator in powers of t are asymptotic rather than convergent. The sums over paths of length n, μ_n, are also the moments of the projected density of states, as can be seen by integrating E^n over $R(E)$ on a contour which encloses the real energy axis of the complex energy plane.

The above expansion of the resolvent as a sum over paths does not converge because the number of paths increases faster than any power of their length. This can be seen in a simple system consisting of two identical orbitals A and B. At each step of a path the choice is to step to the same orbital or to the other orbital. If the step is to the same orbital, then that step contributes a factor of the energy of the orbital v which is the same for both A and B, and if the step is to the other orbital, then the contribution is h, independent of whether the step is from A to B or from B to A. By convention, there is one path of length zero, contributing one to μ_0; there is also one of length one with μ_1 equal to v; two of length two with μ_2 equal to v^2+h^2; and so on. In general, there are 2^{n-1} paths of length n with μ_n equal to $\frac{1}{2}(v+h)^n+\frac{1}{2}(v-h)^n$. As n increases, both the number and contribution of the paths increases exponentially, and since these contributions are divided by just E^n, the path expansion in this example converges only for E sufficiently large that it is uninteresting. For other examples, the series converges nowhere.

In applications of quantum path counting, it is usual to truncate the set of basis orbitals as in the tight-binding approximation where only atomic-like valence orbitals are retained. For example in comparing the electronic states at transition metal surfaces (Haydock *et al.* 1972*b*) needed only the atomic d-orbitals to get a good qualitative picture of surface electronic structure. Atoms on different surfaces of the same transition metal have different coordinations, for example the 111 surface of FCC nickel has coordination 9, while the 100 surface has coordination 8. The lowest moment of path length for which these two surfaces differ is μ_2 which is greater for the 111 surface by the ratio of 9 to 8 relative to the 100 surface. Thus the ratio of the spread in energy of the electronic states at these two surfaces is $(\frac{9}{8})^{\frac{1}{2}}$ and, crudely the ratio of the density of states at the Fermi level is $(\frac{8}{9})^{\frac{1}{2}}$. The reactivity of a metal surface is roughly related to the amplitudes of states at the Fermi level ready to hybridize with the electronic states of a passing atom; so from this simple path counting argument and Fermi's golden rule, one concludes that some sort of zero temperature reaction rate on the two surfaces should be in the ratio of 8 to 9, the ratio of squares of the hybridizing matrix elements.

3. Determinants of paths

An alternative to a series is the continued fraction expansion which from the time of the ancient Greeks has been recognized as a highly convergent approximation scheme. In this approach, the paths are generated from a set of elementary paths, as for example, the paths in above the two orbital system are made up entirely of hops which stay on the same atom and hops which change atoms. This path expansion may be summed to give $1/(E-v-h^2/E)$ which is the first two levels of a continued fraction. If one attempts to extend this idea to a three-orbital system, expressions become much more complicated and a general analysis is necessary.

In the nineteenth century, work on the above moment problem revealed that the elementary quantities from which all the paths could be generated are a set of determinants (Shohat & Tamarkin 1943) which may be expressed in terms of the moments as

$$A_n = \begin{vmatrix} \mu_0 & \mu_1 & \cdots & \mu_{n-1} & \mu_{n+1} \\ \mu_1 & \mu_2 & \cdots & \mu_n & \mu_{n+2} \\ \cdot & \cdot & \cdots & \cdot & \cdot \\ \cdot & \cdot & \cdots & \cdot & \cdot \\ \mu_n & \mu_{n+1} & \cdots & \mu_{2n-1} & \mu_{2n+1} \end{vmatrix}, \tag{3.1}$$

$$B_n = \begin{vmatrix} \mu_0 & \mu_1 & \cdots & \mu_{n-1} & \mu_n \\ \mu_1 & \mu_2 & \cdots & \mu_n & \mu_{n+1} \\ \cdot & \cdot & \cdots & \cdot & \cdot \\ \cdot & \cdot & \cdots & \cdot & \cdot \\ \mu_n & \mu_{n+1} & \cdots & \mu_{2n-1} & \mu_{2n} \end{vmatrix}. \tag{3.2}$$

These determinants consist of sums of products of the moments which in turn are sums of products of the matrix elements of the hamiltonian along paths. Because the same paths occur in many moments in each determinant, there is a great deal of cancellation which makes direct evaluation of the determinants impractical.

The recursion method (Haydock 1980) avoids these determinants by direct tridiagonalization of the hamiltonian. The process begins with a normalized orbital ϕ_0, and generates a new orbital,

$$\phi_1 = (\boldsymbol{H}\phi_0 - a_0\phi_0)/b_1, \tag{3.3}$$

where a_0 and b_1 are chosen to orthonormalize ϕ_1 with respect to ϕ_0. The nth recurrence is,

$$\phi_{n+1} = [(\boldsymbol{H} - a_n)\phi_0 - b_n\phi_{n-1}]/b_{n+1}, \tag{3.4}$$

where a_n and b_{n+1} are chosen to orthonormalize ϕ_{n+1} with respect to ϕ_n. A convergent expansion of the resolvent is given by the continued fraction,

$$R(E) = 1/[E - a_0 - b_1^2/(E - a_1 - b_2{}^2/(E - a_2 - \ldots))], \tag{3.5}$$

from which it follows that these tridiagonal matrix elements generate the moments of the hamiltonian. While this method of constructing the continued fraction is numerically stable, it does not involve any explicit path summation, and so does not give any physical insight into the importance of various physical processes. It is difficult to interpret the parameters other than as matrix elements of an equivalent one-dimensional hamiltonian.

The cancellation between paths in different terms of the above determinants can be made explicit by introducing an artificial time dependence, and by considering groups of paths. Ratios of the determinants are then the parameters of the continued fraction expansion of the resolvent. Think of paths in terms of a step at every tick of a clock. Each step goes from the current orbital to any other orbital including the same one, and multiplies the contribution from the path by the matrix element of the hamiltonian between the two orbitals of the step. The determinant B_0 is defined to be the normalization of ϕ_0, and the determinant A_1 is simply the diagonal matrix element of $\boldsymbol{H}$ for ϕ_0, which we can think of as the contribution from paths which start at ϕ_0 at $t = 0$ and end at ϕ_0 at $t = 1$. The next determinant is B_1, which we may think of as the contribution from pairs of paths which start at $t = -1$ and $t = 0$, finishing at $t = 0$ and $t = 1$, where we now take for granted that paths start and finish on ϕ_0. There are two ways that paths can satisfy this timing: the first is that one path leaves the origin at $t = -1$ and returns at $t = 1$ after two steps while the other path starts and finishes at $t = 0$ with no steps, and the second way is that both paths consist of one step starting at the origin at $t = -1$ and $t = 0$. From the definition of B_1, the first way of starting and finishing the paths contributes with a positive sign while the second is negative because of the permutation of the times of finishing relative to the times of starting. Paths which meet at the same orbital at the same time, contribute to the determinant in two ways, but with opposite sign because of the permutation, and so cancel. For example, in B_1 the pair of paths which stay at the origin from $t = -1$ and $t = 0$, finishing at $t = 0$ and $t = 1$, meet at the origin and contribute with opposite signs depending on the order of finishing.

The $(n+1)$ by $(n+1)$ determinants of B_n or A_n may be expressed as the sum of contributions from groups of $n+1$ paths (Viennot 1989) starting at $t = -n$, $t = -n+1$, …, $t = 0$, and finishing at $t = 0$, $t = 1$, …, $t = n$ for B_n or $t = 0$, $t = 1$, …, $t = n-1$, not $t = n$, but rather $t = n+1$, for A_n. The contribution from one of these groups of $n+1$ paths is the product of the matrix elements for their steps with a sign given by the permutation of the order of finishing relative to first out, last in. Groups of paths which meet on the same orbital at the same time cancel because each meeting allows the group to contribute twice but with opposite sign. Only the groups of paths which never meet actually contribute to the determinant. It is worth noting that because the determinants are the sums of contributions from groups of paths, a perturbation to the hamiltonian produces only a polynomial rather than an infinite series.

In terms of the determinants of mutually avoiding paths, the resolvent is given by the continued fraction equation (3.5) where the parameters are,

$$b_n = [B_{n-2}B_n]^{\frac{1}{2}}/B_{n-1}, \tag{3.6}$$

and

$$a_n = [A_n/B_n]-[A_{n-1}/B_{n-1}]. \tag{3.7}$$

Inverse Fourier transforms of the above continued fractions provide convergent approximants to the Feynman path integrals (Feynman & Hibbs 1965). For example, the matrix element of the propagator from ϕ_0 to ϕ_0 in time t is,

$$\int \exp\{-\mathrm{i}A(P)\}\,\mathrm{d}P = (2\pi\mathrm{i})^{-1}\int \exp(-\mathrm{i}Et)\,R(E)\,\mathrm{d}E, \tag{3.8}$$

where the integral on the left is over all paths P from ϕ_0 at time 0 to ϕ_0 at time t, with the action $A(P)$ appropriate for $\boldsymbol{H}$; and the integral on the right is around a contour in the complex E-plane which encloses the singularities of $R(E)$. The path summations can be viewed as a discretization of the path integral.

4. Transition metal Laves phases and the stability of stacking sequences

As a simple example, consider the bandstructure contribution to the total energy of the FCC structure from the partly filled s-orbitals of metal atoms. This structure consists of spherical atoms in close-packed layers which can stack on top of one another in three equivalent ways. For the ideal HCP structure the layers alternate in

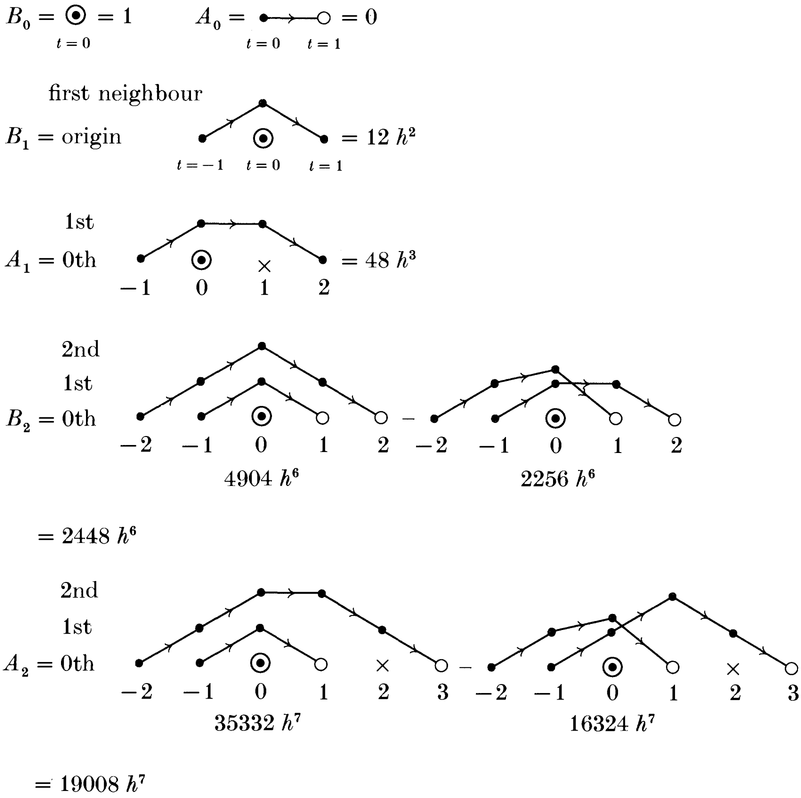

Figure 1. Schematic representations and numbers of the mutually avoiding paths which contribute to the FCC band-structure energy.

position, while for the FCC structure every third layer repeats. The band-structure energy can be calculated from the projected density of states which for the s-orbitals in these structures is also the average density of states because the s-orbitals are all equivalent. The sum of the energies of the occupied states is then the band-structure contribution to the cohesive energy of each structure.

The continued fraction for the projected resolvent and density of states can be calculated using the above method of path counting with a simple hamiltonian which has matrix elements h between nearest neighbour orbitals and zero otherwise. Each orbital has 12 nearest neighbours and 42 second neighbours for the FCC structure. Some of the various kinds and numbers of mutually avoiding paths are shown in figure 1.

Using the relations between the determinants and the continued fraction parameters, equations (3.6) and (3.7), gives an approximate resolvent element,

$$R(E) = 1/[E-12h^2/(E-4h-17h^2/(E-768h/204))]. \tag{3.9}$$

The band-structure energy per atom is then the sum of the residues of this resolvent for the poles corresponding to occupied states, weighted by the energy of each pole.

To investigate the role of d-band electron per atom ratio, the recursion method has been applied to the structural stability of the AB_2 transition metal compounds which form in one of the three Laves phases (Haydock & Johannes 1975; Johannes *et al.* 1976) which are isomorphs of the $MgCu_2$, $MgZn_2$, and $MgNi_2$ structures. Like HCP and

FCC, these compounds may be described by their stacking sequences which a much more complex and repeat every 12th, 8th, and 16th layer respectively. The band-structure contribution to the cohesive energy was calculated as a function of d-band filling for each structure using a hamiltonian derived from canonical d-orbitals scaled to the various atoms.

In this work the continued fraction parameters described above were obtained from recurrences rather than path counting, so it was not possible to identify the electronic processes which account for the structural energy differences. However, the results did demonstrate the importance of the relationship between the local environment of atoms and the symmetry of the atomic orbitals in that the band-structure energy. The differences in band-structure contribution to the cohesive energy calculated using a difference in energy between d-orbitals on the two kinds of atoms which depends quadratically on the group number difference of the atoms, correctly separates the structures of all the 76 known non-magnetic occurrences of such compounds.

5. Conclusion

In the absence of symmetry, the quantum mechanical states of a system can only be determined by direct integration of its equations of motion. Although the power series expansion of the resolvent or propagator in paths does not converge, the continued fraction expansion does, and its parameters can be expressed as ratios of sums of mutually avoiding groups of paths, through which the behaviour of the system can be related to elementary physical processes. Subtle differences in structural energies can be calculated accurately by this means.

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Discussion

N. W. Ashcroft (*Cornell University, U.S.A.*). It is indeed impressive that this reformulation of the recursion method accounts for the subtle energy differences found in systems with quite complex unit cells. Per atom, it would seem that these energy differences are on the scale of a few tens of degrees. Can a simple physical argument be offered that explains why ion dynamics (on the scale of a few hundred degrees in a given structure) is apparently playing so insignificant a role?

R. Haydock. The stable structure is that with the minimum Gibbs free energy, to which the band-structure energy is one contribution. In the case of the transition metal Laves phases, I have argued that the electronic band-structure energy is the dominant contribution giving differences of order 10^{-3} rydberg per formula unit which corresponds to temperatures of hundreds of kelvins at which some of the compounds studied do indeed undergo structural transitions.

As to other contributions to the Gibbs free energy such as the ion dynamics, what matters are again the differences between structures. The phonon spectra could be calculated for the transition metal Laves phases by similar methods to those I have used for the electrons. Their contributions to the free energy is like that of the electrons but scaled by about 10^{-3}, the ratio of electronic to ionic masses. Thus, although the electronic energy differences are of similar size to phonon energies, it is the differences in phonon energies which matter and they are about one thousandth of the differences in electronic energies.