Model Calculation of Stark Ladder Resonances

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A Bloch model Hamiltonian for an electron is an external electric field is solved exactly. This enables a rigorous discussion of the Stark ladder, which has been a controversial subject for some time. It is shown that the Stark ladder states are resonances. An explicit expression for the resonance width is obtained.

There has been interest in a better understanding of the properties of the Schrödinger equation describing the motion of a particle in a solid pervaded by an external field. One problem here is the following: Is there a Wannier-Stark ladder or not?[1-5]

The Wannier-Stark ladder is a periodic structure in the spectrum caused by bound electronic states and is the electric field analog of Landau levels. The picture associated with this quantization is the following: The external field uniformly accelerates the particle in k space. Since the Brillouin zone is topologically a torus, the orbits are closed (periodic), and the energies quantized. It follows that the eigenfunctions are normalizable and the particle is localized in space. Formally, it has been shown that the Stark ladder states are solutions of the Schrödinger equation in the one-band approximation.[1,2] Thus, in the absence of tunneling, the Schrödinger Hamiltonian has bound states. This, however, conflicts with the picture that one has in x space. Bloch waves are extended all over space and it is difficult to see how an external homogeneous field can confine the particle to (essentially) a finite region. On the contrary, the electron is pushed to infinity. Moreover, a theorem in the spectral theory of Schrödinger operators guarantees the absolute continuity of the spectrum and the absence of bound states.[6] This means that the concept of the Wannier-Stark ladder in the strict spectral sense is wrong.

More importantly, the Wannier-Stark ladder has been an experimental problem.[3,5,7] In principle, every measurement of the Franz-Keldysh effect is a measurement of the Wannier-Stark ladder. However, in practically all of these experiments, no periodic structure has been observed and only a few authors have reported seeing the ladder.[7] Since the interpretation of these few experiments is still not unequivocal, the Wannier-Stark ladder is not yet an established experimental fact.

There has been a long-standing controversy on the existence of the Stark ladder. From a theoretical viewpoint, the derivation of the ladder involves uncontrolled approximations.[2] (It is not clear in what sense the one-band Hamiltonian approximates the Schrödinger Hamiltonian.) The ladder may therefore reflect the one-band approximation rather than the physics of the system.

Several attempts have been made to settle the problem.[5,8-11] However, there has been little progress made in a rigorous treatment of the full Schrödinger Hamiltonian. (I do not consider here finite crystal model Hamiltonians where the distinction between bound and extended states is obscured.[9] I felt that a concrete, solvable example would considerable clarify the situation, and may even be more convincing than general but abstract spectral theorems. Such a solvable model is presented here.

In my model, the Wannier-Stark ladder turns out to be a ladder of resonances. More precisely, an analytic continuation of the Hamiltonian to the nonphysical sheet has an infinite set of complex eigenvalues in the form of a ladder lying parallel to the real energy axis. This is in agreement with the infinite extension of the states because the Hamiltonian has no true eigenvalues. On the other hand, this also agrees with the essence of the Wannier-Stark ladder because resonances (if they are sufficiently narrow) are indistinguishable from true bound states. The Stark ladder states are therefore not discrete, stable eigenvalues but metastable states. This verifies the conjecture made by Rauh and Wannier.[12] I feel that this model is an important step in the understanding of the Wannier-Stark ladder effect.

This model also helps to clarify the meaning of "small external field." In fact, since the external field is a singular perturbation (which diverges at infinity) it is not clear in what sense, if any at all, a nonzero field is small.[4,13-16] It turns out that the problem has *two* dimensionless parameters $f=(meEa^3/\pi^3)^{1/2}$ and $u=v^2m/2eEK$. E is the external field, $K=2\pi/a$ the unit reciprocal-lattice vector, and v the strength of the potential. Neither f nor u depends on the size of the crystal (in the model the crystal is infinite). Thus, even though the external field is a singular perturbation, the meaning of small E is $f \ll 1$ and $u \gg 1$. Since $E_{\rm cgs} = 1.72 \times 10^7 E_{\rm a.u.}$, in most cases of practical interest, the external field is indeed weak in the above sense.

A solvable model necessarily involves a special choice of the crystal periodic potential V. This choice must, however, be such that it has all the elements of the Stark ladder problem. Let us therefore isolate the two central features of the problem: (a) The Bloch model Hamiltonian must have energy gaps (clearly there is no Stark ladder for $V=0$). (b) The spectrum for $E \neq 0$ must be continuous from $-\infty$ to $+\infty$, having no true eigenvalues. V will be chosen subject to these two conditions.

A general periodic potential V commutes with the lattice translation operator. In momentum space this means

$$e^{ipa}V(p,p')e^{-ip'a} = V(p,p').$$

Hence, $V(p,p')=0$, unless $p-p'$ is a reciprocal-lattice vector. [For local potentials, $V(p,p') = V(p-p')$.] Since a Stark ladder is associated with each isolated band, an obvious simplification is to choose V such that the Bloch Hamiltonian has a single gap. An easy way to accomplish this is by nonlocal potentials. The model potentials that I shall consider is

$$V(p,p') = v[\delta(p-p'+K)\chi_{0,K}(p') + \delta(p-p'-K)\chi_{-K,0}(p')], \tag{1}$$

where $\chi_{ab}(x)$ is the characteristic function of the interval $(a,b]$, i.e., $\chi_{ab}(x)=1$, $a<x\leq b$ and zero elsewhere. V is manifestly periodic. The lowest band of the corresponding Bloch Hamiltonian is given (with $q=K-|k|$) by

$$\epsilon(k) = \frac{k^2+q^2}{4m} - \left[\left(\frac{k^2-q^2}{4m}\right)^2 + v^2\right]^{1/2} \quad |k| < \frac{K}{2}, \tag{2}$$

for which the band gap is $2v$.

In the presence of an external homogeneous electric field of strength $\epsilon = eE$, the Hamiltonian is

$$H_\epsilon = -\epsilon x + p^2/2m + V. \tag{3}$$

I shall investigate the second-sheet structure of H_ϵ. Resonances are poles of the resolvent on the nonphysical sheet.[17-19] True eigenvalues are real poles. Note that (a) the time evolution associated with the spectral projection on the poles decays exponentially with the right time constant and (b) the analytic continuation of the scattering amplitude has poles (Wigner-Weisskopf resonances) at energies where the resolvent has its poles.[17]

In order to analytically continue (3) to the nonphysical sheet, let us rewrite the eigenvalue equation for the eigenvalue λ so that

$$\psi(p) = R_\epsilon(\lambda)V\psi(p), \tag{4}$$

where $R_\epsilon(\lambda)$ is the resolvent of $-\epsilon x + p^2/2m$.[14] And we have

$$R_\epsilon(\lambda) = -(i/\epsilon)e(-p)e(p')\theta(p-p') \quad \mathrm{Im}\lambda > 0,$$
$$e(p) = \exp[-i(\lambda p - p^3/6m)/\epsilon]. \tag{5}$$

$R_\epsilon(\lambda)$ has a cut along the λ axis. Equation (5) gives a natural analytic continuation of (4) to the nonphysical sheet, which is obtained by using Eq. (5) also for $\mathrm{Im}\lambda < 0$.

Equation (4) has only the trivial solution, $\psi \equiv 0$, (in L^2) for $\mathrm{Im}\lambda > 0$, because of self-adjointness. As we shall see, Eq. (4) has nontrivial (L^2) solutions for $\mathrm{Im}\lambda < 0$. These are resonances, and they turn out to have a ladder structure. Moreover, since $\mathrm{Im}\lambda < 0$, there are no true bound states and the spectrum of H_ϵ is absolutely continuous, as it should be.

Let us introduce the notation (with terms matching at corresponding positions)

$$\psi\chi_{-\infty,-K} + \psi\chi_{-K,0} + \psi\chi_{0,K} + \psi\chi_{K,\infty} = \psi_{-\infty} + \psi_- + \psi_+ + \psi_\infty. \tag{6}$$

Equation (4) then reads

$$\Psi_{-\infty}(p) = 0, \tag{4$'$a}$$

$$e(p)\Psi_-(p) = -\frac{iv}{\epsilon}\int_{-K}^{P} e(p')\Psi_+(p'+K)dp', \tag{4$'$b}$$

$$e(p)\Psi_+(p) = e(0)\Psi_-(0) - \frac{iv}{\epsilon}\int_0^P e(p')\Psi_-(p'-K)dp', \tag{4$'$c}$$

$$e(p)\Psi_\infty(p) = e(K)\Psi_+(K). \tag{4$'$d}$$

Equation (4$'$d) and the requirement of square-integrability imply $\Psi_\infty(p)=0$. If we let $\varphi_\pm = e(p)\psi_\pm(p)$, the solution of Eq. (4$'$) satisfying the appropriate boundary conditions (details of the calculations will be presented elsewhere) is then given by

$$\varphi_+(p) = \exp\left[\frac{i}{4m\epsilon}\left(p^2K - pK^2\right)\right]Y_+\left(\left(p-\frac{K}{2}\right)\frac{2}{Kf}\right),$$

where

$$Y_+(x) = H_0(1/f)H_e(x) - H_e(1/f)H_0(x),$$
$$H_e(x) = e^{-ix^2/2}F(iu|\tfrac{1}{2}|ix^2), \qquad (7)$$
$$H_0(x) = e^{-ix^2/2}xF(\tfrac{1}{2}+iu|\tfrac{3}{2}|ix^2).$$

The parameters f and u were defined in the introduction; $F(a|c|z)$ is the confluent hypergeometric function; H_e and H_0 are the even and odd solution of the complex harmonic oscillator. The eigenvalue equation follows from the continuity of the wave function at $p=0$, i.e., $\varphi_-(0)=\varphi_+(0)$. Let

$$2r(\epsilon)e^{i\theta(\epsilon)} = iu^{-1/2}H_e(1/f)[\int_0^{1/f} e^{-ix^2/2}H_e(x)dx]^{-1}.$$

Then, the eigenvalues of Eq. (4) are

$$\lambda_n = i\epsilon/K \ln|r(\epsilon)| + \epsilon/K(\theta+2\pi n) + 5K^2/48m, \qquad (9)$$

where n is an arbitrary integer. The spectrum of eigenvalues therefore has the form of a ladder. An asymptotic estimate of $r(\epsilon)$ gives[20]

$$|r(\epsilon)| = [1+1/(4f^2u)]^{1/2}[1+O(\epsilon)], \qquad (10)$$

and $|r(\epsilon)|>1$, as it should (i.e., $\mathrm{Im}\lambda<0$). Equation (9) describes resonances in the form of a ladder which lies parallel to the real axis on the nonphysical sheet. The width of the ladder states is independent of n and is given by

$$\Gamma = (a\epsilon/2\pi)\ln|r(\epsilon)|. \qquad (11)$$

The ratio of Γ to the level spacing becomes constant as $\epsilon\to 0$. The spacing between the resonances is ϵa. This is the Wannier-Stark ladder.[1]

The Stark ladder is observable provided $\Gamma \ll \epsilon a$; and

$$fu^{1/2} = 2vm/K^2 \gg 10^{-3}. \qquad (12)$$

This is interpreted as a requirement of a minimal gap (relative to the band width). Such a condition was known to be important for the observability of the ladder.[2] (The relatively small constant, 10^{-3}, however, is a new result.)

To conclude, let us consider how the above result transfers to the case of local periodic potentials. In the absence of tunneling, the Stark ladder of the one-band Hamiltonian is embedded in the spectrum of the other bands. It is not difficult to see that the latter is continuous, so the interband interaction is a perturbation of embedded eigenvalues[17] (i.e., eigenvalues embedded in a continuous spectrum). Contrary to isolated eigenvalues which are stable in general (i.e., stay on the real energy axis), embedded eigenvalues are unstable in general. A small perturbation gives purely continuous spectrum by shifting the eigenvalues to the nonphysical sheet.[17] Thus, the interband interaction makes the Stark ladder states resonances. Hence, the qualitative features of the model presented above transfer also to local potentials. On the other hand, it is more difficult to speculate on the functional form of $\Gamma(\epsilon)$. Γ is clearly model-dependent. In particular, since my model has bad analytic properties (due to the characteristic function in V) it gives no indication on $\Gamma(\epsilon)$ for local potentials. A natural conjecture following from the Fermi golden rule is that $\Gamma(\epsilon)$ is exponentially small as $\epsilon\to 0$.[21,22] Whether this conjecture can be made into a theorem still remains to be seen.

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[1]G. H. Wannier, Phys. Rev. 117, 432 (1960), and Phys. Rev. 181, 1364 (1969), and Rev. Mod. Phys. 34, 645 (1962).

[2]J. Zak, Phys. Rev. 181, 1366 (1969), and Phys. Rev. Lett. 20, 1477 (1968), and also in *Solid State Physics*, edited by H. Ehrenreich (Academic, New York, 1972), Vol. 27.

[3]L. Fritsche, Phys. Status Solidi 13, 487 (1966); W. Franz, Phys. Status Solidi 1, K4 (1961).

[4]A. Rabinovitch, Phys. Lett. 33A, 403 (1970), and Phys. Lett. 48A, 149 (1974); A. Rabinovitch and J. Zak, Phys. Rev. B 4, 2358 (1971).

[5]H. Fukuyama, R. A. Bari, and H. C. Fodgby, Phys. Rev. B 8, 5579 (1973); V. S. Vavilov, V. S. Chanbarisov, and V. B. Stopachinskii, Fiz. Tverd. Tela (Leningrad) 8, 2660 (1966) [Sov. Phys. Solid State 8, 2126 (1967).

[6]J. Avron, J. Zak, A. Grossmann, L. Gunther, to be published.

[7]R. W. Koss and L. M. Lambert, Phys. Rev. B 5, 1979 (1972). See also A. Rauch and G. H. Wannier, Solid State Commun. 15, 1239 (1974), and Ref. 2 for additional references.

[8]C. A. Moyer, Phys. Rev. B 7, 5025 (1973).

[9]S. G. Davison, Phys. Lett. 43A, 117 (1973); S. G. Davison and K. P. Tan, Z. Phys. 251, 6 (1972).

[10]W. Shockley, Phys. Rev. Lett. 28, 349 (1972).

[11]In subsequent work I intend to present a general proof of the main results of the paper.

[12]Rauh and Wannier, Ref. 7.

[13]G. H. Wannier and J. P. Van Dyke, J. Math. Phys. (N.Y.) 9, 899 (1968).

[14]J. Avron and J. Zak, Phys. Rev. B 9, 658 (1974).
[15]H. Bross and H. Weilacher, Z. Phys. 255, 325 (1972).
[16]A. Rabinovitch, Phys. Rev. B 4, 1017 (1971).
[17]B. Simon, Ann. Math. 97, 247 (1973).
[18]R. Peierls, in *Proceedings of the Ninth International Conference on Physics of Electrons Atomic Collisions, Seattle, Washington, 1975*, edited by J. S. Risley and R. Geballe (Univ. of Washington Press, Seattle, 1975).
[19]A. Grossman, J. Math. Phys. (N.Y.) 5, 1025 (1964).
[20]F. W. J. Olver, J. Res. Nat. Bur. Stand., Sect. B 63, 131 (1959).
[21]C. Zener, in *Mathematical Physics in One Dimension*, edited by Elliot Lieb and Daniel C. Mattis (Academic, New York, 1966).
[22]R. Peierls, private communication.

NMR Relaxation in the Superionic Conductor β-$LiAlSiO_4$†

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NMR T_1's are reported for ^7Li and ^{27}Al in β-$LiAlSiO_4$ which show a frequency-independent minimum as a function of temperature. The anomalous frequency independence is interpreted in terms of highly correlated one-dimensional Li^+ motion together with an order-disorder transition believed to occur above 500°C.

Ionic motion in superionic conductors is a phenomenon[1] of much intrinsic interest as well as having important technological implications for solid-state batteries. These compounds are characterized by a large, temperature-independent number of vacancies which provide paths of high ionic mobility. The crystal structure is often such that the paths are restricted in dimensionality, as for the one-dimensional (1D) conductor β-$LiAlSiO_4$ ($LiAlSiO_4$ with the β-eucryptite structure) studied here. These features can cause significant differences in the character of ionic diffusion from that encountered in the more widely studied cases of a small number of vacancies in a 3D lattice. In the Letter we present data on the NMR spin-lattice relaxation times T_1 of ^{27}Al and ^7Li in β-$LiAlSiO_4$ which show striking departures from the usual behavior expected for diffusion, and interpret them in terms of highly correlated 1D motion together with an order-disorder transition believed to occur in the compound.

The crystal structure[2] of β-$LiAlSiO_4$ is such that the Al^{3+}, Si^{4+}, and O^{2-} ions form a hexagonal lattice (similar to that of β-quartz) with channels parallel to the c axis in which the Li^+ ions reside. There are twice as many Li^+ sites as there are ions present which should permit the Li^+ ions to diffuse along the channels. High conductivity has been observed in glass ceramics and single crystals of these materials,[3] although the degree of anisotropy in the single crystal is as yet unknown.

At room temperature, x-ray studies[2] show that the Li^+ ions order, occupying alternating sites either in the planes of the Al^{3+} ions or in the Si^{4+} planes. Above 400°C the ordering is strongly reduced, disappearing somewhere above 460°C with a proposed order-disorder transition.

T_1's of the fixed-lattice ^{27}Al nucleus and of the diffusing ^7Li nucleus from polycrystalline ceramic samples are shown in Fig. 1 as a function of inverse absolute temperature. The 20-MHz ^7Li T_1's are taken from the data of Weaver and Bie-

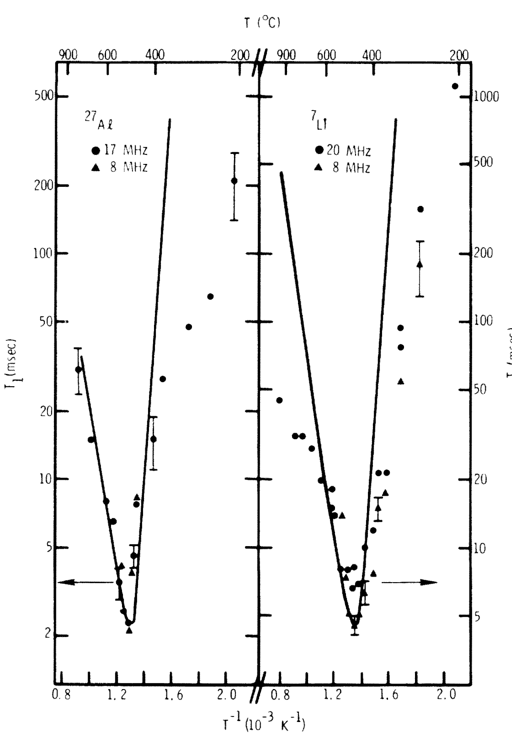

FIG. 1. ^{27}Al and ^7Li relaxation times. Solid curves are theoretical, scaled to give proper T_1 at minimum, and with other parameters as described in text.