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Sign of the effective tunneling parameters in paraelectric systems

Frank Bridges
University of California at Santa Cruz, Santa Cruz, California 95064
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Although the tunneling parameter for a single pair of potential wells is usually assumed to be negative, in more complex potential well systems some of the smaller *effective* parameters obtained experimentally appear to be positive. Here it is shown that the neglect of overlap parameters and upper excited states can lead to positive effective parameters. Similar results can also be obtained if the tunneling parameters are actually complex but are treated as real quantities.

I. INTRODUCTION

In studies of paraelectric and paraelastic tunneling systems over the last decade, it has been assumed that all of the tunneling elements are intrinsically negative,[1] although no detailed discussions of this point have been made. However, recently the second-nearest-neighbor *effective* tunneling element for the KCl:CN$^-$ system was found to be *positive*[2] and similar results[3] may also apply for KBr:Li$^+$. It is therefore important to understand what is meant by an *effective tunneling parameter* and how it can be positive in some cases.

In all tunneling models, several assumptions are basic and common.[1,4] Consider l adjacent potential wells arranged according to the symmetry of the system. For example, see Fig. 1 for $l=2$ and 4 systems. If a particle is placed in one of the wells, its wave function is assumed to extend into the other wells (i.e., the potential barriers are not infinite) and the particle has a finite probability at some later time of being in one of the other wells. This problem[1] is parametrized by introducing tunneling elements of the form

$$(H_c)_{ij} = \langle i\,|H_c|\,j\rangle, \quad i \neq j \tag{1}$$

where H_c is the crystal-field Hamiltonian and $|i\rangle$ is the wave function for the particle to be in the ith potential well. Clearly the set of states $|i\rangle$ is not orthogonal since the wave functions from neighboring wells $|j\rangle$ are not necessarily zero in the ith well. Consequently (small) overlap integrals of the form

$$S = \langle i|j\rangle, \quad i \neq j \tag{2}$$

should be included, as was done by Gomez *et al.*[1] for the case of no external fields. However, this also *doubles* the number of parameters.[4,5] Since S is expected to be very small, it has usually been assumed to be zero in the analysis of most, if not all, systems. In this approximation, the eigenenergies are given in terms of the tunneling elements $(H_c)_{ij}$ $(i \neq j)$ and for systems with high symmetry only a few distinct elements are needed. For example, an eight-potential well system with wells in the directions of the corners of a cube (XY_8 system) has three parameters η, μ, ν.

If one considers the simplest case — that of two potential wells — then one can write an effective Hamiltonian[1] using the nonorthogonal basic states $|i\rangle$ in the form

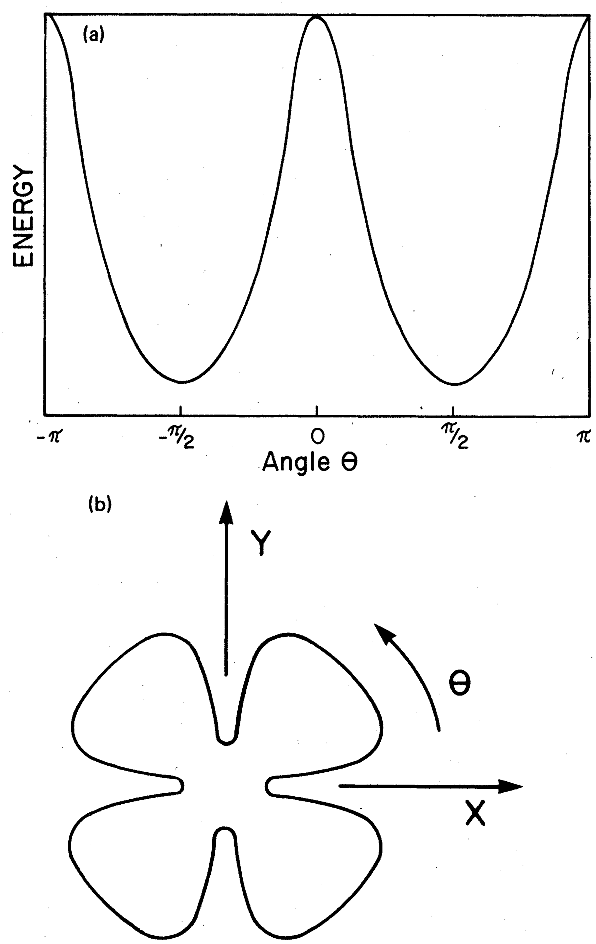

FIG. 1. Potentials for (a) a two-well and (b) four-well planar system. In (b) energy increases radially.

$$H_c = \begin{vmatrix} E_0 & \eta - S_\eta E \\ \eta - S_\eta E & E_0 \end{vmatrix}; \quad H_c\psi = E\psi\,, \tag{3}$$

where

$$E_0 = \langle i | H_c | i \rangle,$$
$$\eta = \langle 1 | H_c | 2 \rangle, \tag{4}$$
$$S_\eta = \langle 1 | 2 \rangle.$$

E_0 is the ground-state energy in each well (neglecting tunneling) and when the tunneling approximation is valid, it is assumed to be orders of magnitude larger than the tunneling parameter η. Neglecting S_η, one can calculate η using some approximation method such as the Wronskian method of Landau and Lifshitz[6] and show that in this case η is negative. Implicit in such a calculation is the assumption that the effects of other higher energy levels can be ignored.

Within such assumptions, we might argue that *all* the tunneling parameters of a more complicated l-well *paraelectric* system should also be negative. Choose any two potential wells of the system. Now apply an electric field perpendicular to a line connecting the two wells such that all other potential wells have a different energy as a result of the electric dipole interaction $-\vec{p}\cdot\vec{E}$. If $\vec{E}$ is large enough, then only the two original states are still degenerate in the absence of tunneling and we can treat these two states as an effective two-well system. Consequently, the tunneling element between these two wells should be negative. Further, since the field is applied perpendicular to the line between the wells, the effects of a large field on these wells is expected to be small. Since one can do this for any pair of wells, one might then argue that all tunneling elements are negative. Thus, it is important to understand how *positive effective parameters* can arise.

II. EFFECTIVE TUNNELING PARAMETERS

The "effective" tunneling parameters are based upon the equations for the zero-field energies of a tunneling system when the overlap parameters S are neglected. For example, the two-well system has zero-field energies $E_0 \pm \eta$ while the four-well system of Fig. 1 has zero-field energies $E_0 + 2\eta + \mu$, $E_0 - 2\eta + \mu$, and $E_0 - \mu$. (six-, eight-, and twelve-well systems are treated in Ref. 1.) Note that in all cases, E_0 is an additive constant to each of the tunneling energy levels. Since only the relative splittings are measured, E_0 is usually taken to be zero and the measured splittings can be used to calculate *effective parameters* η *and* μ *which parametrize the experimental zero-field energy levels*. However, they are effective parameters in the sense that the η and μ obtained in this manner will include some (usually small) contributions from the overlap parameters and also perhaps some small contributions from higher energy levels. Both of these effects can lead to the possibility that in systems with more than one tunneling parameter, the smaller tunneling elements can be positive. Yet a third way in which an apparent positive tunneling parameter might arise occurs if the tunneling parameters are actually complex, but are treated as real parameters. We discuss each in turn.

III. EFFECT OF THE OVERLAP PARAMETERS

To demonstrate the effect of the overlap parameters, we consider the six-well system with potential wells along the $\pm x$, $\pm y$, and $\pm z$ axes. Gomex *et al.* have calculated the zero-field energies of this system[1] including the overlap parameters and obtain

$$E_1 = \frac{E_0 + 4\eta + \mu}{x}; \quad x = 1 + 4S_\eta + S_\mu \tag{5}$$

$$E_2 = \frac{E_0 - 2\eta + \mu}{y}; \quad y = 1 - 2S_\eta + S_\mu \tag{6}$$

$$E_3 = \frac{E_0 - \mu}{z}; \quad z = 1 - S_\mu \tag{7}$$

where η is the nearest-neighbor tunneling element, $\langle x | H_c | y \rangle$, μ is the 180° element $\langle -x | H_c | x \rangle$, S_η is the nearest-neighbor overlap parameter $\langle x | y \rangle$, and S_μ is the 180° overlap parameter $\langle -x | x \rangle$.

To describe these energies in terms of *effective* parameters we must write

$$E_1 = F + 4\eta' + \mu'\,, \tag{8}$$

$$E_2 = F - 2\eta' + \mu'\,, \tag{9}$$

$$E_3 = F - \mu'\,. \tag{10}$$

Then the observed zero-field splittings can be expressed in terms of the *effective* parameters η' and μ'. Here F is an additive constant for each level — as E_0 was for the case S_η, $S_\mu = 0$ — and is not an important parameter if only the tunneling energies are investigated. Equations (5)–(10) represent three linear equations in three unknowns, F, η', and μ', and can be easily solved to give

$$F = \frac{1}{2}\left[\frac{E_0}{3}\left(\frac{1}{x} + \frac{2}{y} + \frac{3}{z}\right) + \frac{4}{3}\eta\left(\frac{1}{x} - \frac{1}{y}\right) + \frac{\mu}{3}\left(\frac{1}{x} + \frac{2}{y} - \frac{3}{z}\right)\right], \tag{11}$$

$$\eta' = \frac{\eta}{3}\left(\frac{2}{x} + \frac{1}{y}\right) + \frac{1}{6}\left(\frac{1}{x} - \frac{1}{y}\right)(E_0 + \mu), \tag{12}$$

$$\mu' = \frac{\mu}{6}\left(\frac{1}{x} + \frac{2}{y} + \frac{3}{z}\right) + \frac{E_0}{6}\left(\frac{1}{x} + \frac{2}{y} - \frac{3}{z}\right) + \frac{2\eta}{3}\left(\frac{1}{x} - \frac{1}{y}\right). \tag{13}$$

Thus, although in principle, there are four parameters in Eqs. (5) – (7), (η, μ, S_η, and S_μ) *the zero-field energies can be parametrized in terms of only two parameters*, η' and μ'. The energies, in terms of these parameters, have the same algebraic form as that obtained when the overlap parameters are ignored. Further, if we assume that μ is very small (or even zero) and η is large (and negative) then μ' *may be positive* (S_μ, S_η are positive). For example, if $\mu \simeq 0$ and $S_\mu \ll S_\eta \ll 1$ such that $E_0 S_\mu \ll |\eta| S_\eta$, then $\mu' \simeq -4\eta S_\eta$ for the sixfold system. Here μ' is clearly positive. Similar results are obtained for other systems. Of course, it should not be assumed that the only two parameters actually needed to parametrize the system are η' and μ'. For example, for paraelectric systems, there is also the dipole moment. However, instead of one dipole-moment parameter, there can in principle be several slightly different dipole parameters: the "real" dipole moment p divided by different factors involving the overlap elements. These calculations are more involved and require a transformation of the XY_6 Hamiltonian to one in which the diagonal elements are the energies E_1, E_2, and E_3, and the off-diagonal elements involve the various different dipole-moment parameters and the external electric field. These results, along with the calculations for the eight- and twelve-potential wells will be given in a separate paper.

Since one experiment has given a positive tunneling parameter for a $\langle 111\rangle$ system, it is instructive to ask how large the overlap parameter(s) must be to explain this result. For such systems there are three tunneling parameters η, μ, ν, and three overlap parameters. If we assume μ, ν, S_μ, and S_ν are zero, then

$$\mu' \simeq 2E_0 S_\eta^2 - 2\eta S_\eta, \quad S_\eta \ll 1. \tag{14}$$

Taking the experimental values[2] $\eta' = -19.45$ GHz, $\mu' = +1.7$ GHz, then $S_\eta \leqslant 0.045$ over a range of values for E_0 around 10 cm^{-1}. This is still fairly small, but is clearly not negligible.

IV. THE NEGLECT OF HIGHER EXCITED STATES

It is clear that if the excited states of the system are not too far away in energy, some observable shifts of the tunneling energy levels can occur. This was pointed out earlier in an explicit calculation in which the coupling of two multiplets of tunneling levels was considered.[7] In the absence of any knowledge of the upper levels one would attempt to parametrize the system using the effective tunneling parameters, but clearly the magnitude of the smaller parameters may include a large contribution from the coupling to the excited states and might again be positive. As an example, consider an XY_6 system for which $\eta \neq 0$, $\mu = 0$, and for which S_η and S_μ can be safely ignored. Then the energy levels will be in the order shown in Fig. 2 (η is negative). If the next highest energy level has T_{1u} symmetry, it will depress the T_{1u} tunneling level by some small amount Δ, as shown by the dotted line, but will not affect the E_g or A_{1g} states.

Consequently the observed levels will be (Δ is a positive quantity)

$$+2|\eta|, \; -\Delta, \; -4|\eta|. \tag{15}$$

Using Eqs. (8) – (10) to define the effective tunneling parameters, one obtains

$$F = -\frac{\Delta}{2}(+E_0), \tag{16}$$

$$\eta' = \eta \quad \text{(negative)}, \tag{17}$$

$$\mu' = +\frac{\Delta}{2} \quad \text{(positive)}. \tag{18}$$

Thus, in such a situation, an effective positive tunneling parameter would again occur.

V. COMPLEX TUNNELING PARAMETERS

Finally to emphasize that positive effective parameters can arise in many ways, we note briefly a third way in which such effects might occur. This arises for some *restricted cases* of lowered symmetry if the tunneling parameters are complex, but are treated as real quantities. This does not correspond to any of the well known paraelectric systems but might occur if a second impurity is involved. [Such a situation was in fact considered[3] (and rejected) as a possible explanation of the spectra for KBr:Li$^+$.] In the presence of a nearest-neighbor impurity atom X the symmetry is reduced (to C_{4v} for the NaCl structure) and the different wells are no longer equivalent,

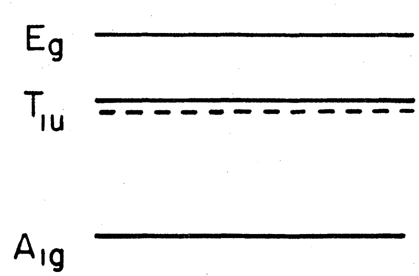

FIG. 2. Energy levels for a $\langle 100\rangle$ (XY_6) model with the 180° tunneling parameter μ set equal to zero. The solid lines are the levels when upper excited states are totally neglected. The dotted line indicates schematically how the T_{1u} state moves down if the next lowest state above the ground-state multiplet is also a T_{1u} state.

leading to the possibility of complex parameters.

First we must show that for the case of full symmetry the matrix elements are indeed real. Consider a set of l equivalent potential wells arranged symmetrically about some origin. Then under all the symmetry operations of the system, well i can be interchanged with any of the other wells j. Since the Hamiltonian remains invariant under such an operation,

$$H_{ij}=H_{ji} \text{ for all } i,j$$

and H_{ij} must be real. If, however, the symmetry is lowered such that under the remaining symmetry operations well i is never rotated to position j, then H_{ij} need not equal H_{ji} and these quantities could indeed be complex.[8] If such a system is analyzed assuming real matrix elements, the smaller effective tunneling parameters can appear positive. As a simple concrete example, consider a three-well system obtained by removing the well at $-x$ in Fig. 1(b), i.e., this well may disappear because of the presence of another impurity. Under reduced C_{2v} symmetry, well $|x\rangle$ is never interchanged with wells $|y\rangle$ or $|-y\rangle$. Consequently, the matrix elements can have the form

$$\mu=\langle y|H|-y\rangle=\mu_0 e^{i\pi} \text{ (real and negative)}, \tag{19}$$

$$\eta=\langle y|H|x\rangle=\langle -y|H|x\rangle=\eta_0 e^{i\theta}. \tag{20}$$

The energy (ϵ) eigenvalue equation is easily found to be

$$\epsilon^3-(\mu_0^2+2\eta_0^2)\epsilon-2\eta_0^2\mu_0\cos(2\theta-\pi)=0. \tag{21}$$

Note that the only term which would involve the effective sign of the tunneling parameter is the last term. All others have the tunneling parameters squared. If θ is taken to be π (the usual assumption) then η is negative and the term

$$-2\eta_0^2\mu_0\cos(2\theta-\pi)$$

is positive. However, if θ is such that $\cos(2\theta-\pi)$ is positive, then this term is negative. Such a situation might be interpreted as a positive value of μ if experimental data are analyzed under the assumption of real tunneling parameters.

VI. SUMMARY

Small positive (effective) tunneling parameters can arise in a variety of ways. However, in each case considered, the dominant parameter must be negative if the symmetric A_{1g} state is to be the ground state. The relative importance of the various mechanisms will depend on the situation under study. In particular, for shallow potential wells, the neglect of the overlap parameter may be the most important.

ACKNOWLEDGMENTS

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[3]R. Russell, Ph.D. thesis, University of California, Santa Cruz, 1978 (unpublished).

[4]F. Bridges, Crit. Rev. Solid State Sci. 5, 1 (1975).

[5]For each of the m distinct tunneling parameter $(H_c)_{ij}$ there is a corresponding overlap parameter S_{ij}. The energies given by Gomez *et al.* (Ref. 1) are expressed in terms of these $2m$ parameters.

[6]L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Addison-Wesley, Reading, Mass., 1958), p. 177.

[7]F. Bridges, Phys. Status Solidi 65, 743 (1974).

[8]The application of an electric field or a uniaxial stress reduces the symmetry such that some sets of wells are inequivalent. Although at low fields the tunneling and electric-field Hamiltonians are considered to be independent, this will not be true at high electric fields. Then one might expect both the phase and the magnitude of some of the tunneling parameters to change.