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Toward a Best Adiabatic Potential

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The concept of a best adiabatic potential is discussed. It is emphasized that it should be best for a number of states, not just for a single state. One particular figure of merit is introduced and applied to a simple model.

Key words: Adiabatic potential.

Recently the concept of a best adiabatic potential has been discussed from several points of view ([1] and references there; also [2]). Denoting the electronic coordinates by y and the nuclear coordinates by Y, then given an electronic wave function $\phi(y, Y)$ normalised according to

$$\int dy|\phi|^2 = 1 \tag{1}$$

one determines an optimal nuclear wave function $\theta(Y)$ by use of the trial function

$$\psi(Y, y) = \theta(Y)\phi(y, Y) \tag{2}$$

in the familiar variation method. The result is of course, assuming that ϕ is real up to Y independent factors, that θ should be an energy eigenfunction in the adiabatic potential U produced by ϕ:

$$U = \int dy\, \phi^* H \phi \tag{3}$$

where H is the total Hamiltonian. The question then is, is there some best choice for ϕ? The standard adiabatic approximation specifies that ϕ should be an

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eigenfunction of the fixed nuclei problem, but it is natural to ask, can one do better?[1]

First let us note that since [3, 4] any function of Y and y can be written in the form (2) (with (1)) it follows that if one tries [5] to determine both θ and ϕ using the usual variation method then, assuming complete flexibility, the result can only be that ψ should be an exact eigenfunction. Now for the ground state this may be a satisfactory result. However this is not the case in general for excited states since it has been shown ([1] In an appendix we give a simple argument leading to the same conclusions.) that the resulting θ has a very non-intuitive form – it has no nodes for finite Y – and the associated U is correspondingly peculiar.

Moreover such an approach will almost inevitably lead to different U's for different states whereas we would suggest, and indeed emphasize, that the notion of a best adiabatic approximation should also include the requirement that the same U should generate a whole set of nuclear states.

One way which suggests itself to implement this idea is, instead of, say, minimizing the energy of a single state (and this, as we have noted, if carried through completely, will produce the exact ground state), to minimize the sum of the energies of the first N states. Thus we should minimize

$$J_N = \sum_{n=0}^{N-1} \int dY \int dy\, \theta_n^* \phi H \theta_n \phi \tag{4}$$

with respect to the θ_n (assuming the θ_n are orthonormal this *does* just lead to the result that they should be the N lowest eigenfunctions in the potential U provided by ϕ), *and* with respect to ϕ (More generally one might weight the terms in (4) with positive weights.).

To test this idea we have used the same coupled oscillator model employed by other authors ([2], [3], [6])

$$H = -\frac{\partial^2}{\partial y^2} - \frac{1}{M}\frac{\partial^2}{\partial Y^2} + y^2 + Y^2 + \alpha y Y \tag{5}$$

where M, the "nuclear" mass is assumed to be very large, and where α is a constant. The exact eigenfunctions and eigenvalues are easily found, and we will concentrate attention on those which have the (almost wholly) electronic normal coordinate in its ground state.[2]

As a first remark let us note that in [6] the U, there called U_0, derived from the exact ground state eigenfunction is assumed *à priori* to be the best adiabatic potential. However though it gives the exact ground state energy, one finds that

[1] Given any set of energy levels one can always find a potential U (in fact many potentials) which will match them exactly. However, in the present context, this still leaves the question which we will not discuss further, can it be written in the form (3)?

[2] Even for quite high excitation of the (almost wholly) nuclear normal coordinate these are still the lowest states of the system and hence [7] our approximate eigenvalues will be upper bounds to these exact energies.

for the first excited state and for all higher states it yields a less accurate energy than the standard adiabatic potential, there called U_0'. Thus from the point of view of the present paper U_0' is a better potential than U_0.

Turning now to the use of J_N, to get some experience we have considered

$$\phi = \left(\frac{1}{\pi}\right)^{1/4} e^{-\frac{1}{2}(y+BY)^2} \tag{6}$$

where B is a real variational parameter ($B = \alpha/2$ yields the standard adiabatic approximation). One then readily finds that

$$U = \left(1+\frac{B^2}{2M}\right) + (1-\alpha B + B^2)Y^2. \tag{7}$$

(Note that the force constant is positive for all B provided that $|\alpha| < 2$ which we will henceforth assume.). U yields eigenvalues

$$E_n = \left[\left(1+\frac{B^2}{2M}\right) + \left(\frac{1-\alpha B+B^2}{M}\right)^{1/2}\right] + 2n\left(\frac{1-\alpha B+B^2}{M}\right)^{1/2} \tag{8}$$

from which it follows that

$$J_N = N\left(1+\frac{B^2}{2M}\right) + N^2\left(\frac{1-\alpha B+B^2}{M}\right)^{1/2}. \tag{9}$$

Setting $\partial J_N/\partial B = 0$ then yields as the equation for the optimal B

$$\frac{B}{M^{1/2}} + \frac{1}{2}\frac{(2B-\alpha)N}{(1-\alpha B+B^2)^{1/2}} = 0. \tag{10}$$

Evidently for $N \to \infty$ it yields

$$B = \alpha/2, \tag{11}$$

i.e. the standard adiabatic result. However for any finite N, (10) will yield a different value for B, one which will in turn yield a smaller J_N than provided by (11) and hence, to that extent, a better U. If one examines the levels in more detail one finds that, through order $M^{-3/2}$, the order in which differences first appear, if $N < N'$ then $E_n(N)$, the nth eigenvalue gotten using J_N, is smaller than $E_n(N')$, and hence[2] a better approximation to the exact E_n, provided that

$$n < NN'/N + N'. \tag{12}$$

Thus in particular the $E_n(N)$ are individually more accurate than the standard adiabatic ones for $n < N$. However we should also note that the standard adiabatic potential always gives better level spacings.

We have also looked briefly at a more complicated trial function

$$\phi = \left(\frac{A}{\pi}\right)^{1/4} e^{-(A/2)(y+BY)^2} \tag{13}$$

with two variational parameters A and B. Here we will note only that though again for $N \to \infty$, B takes on the value $\alpha/2$, A does *not* become 1.

It would be nice to say in conclusion that we have given a definitive answer to the question of determining the optimal U: minimize J_N. However quite apart from this still leaving open the question of what N to choose, there is also the possibility, as mentioned earlier, of replacing J_N by other figures of merit. Nevertheless we think that what we have done does serve to make the point that however one defines a best potential, it should be in that sense best for a number of levels, not just one.

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Appendix

It seems plausible (note that the proof in [1] requires that one overlooks the possibility of a coincidence – see following their Eqs. (21) and (21′) – i.e. it is also a plausibility argument) that because of the coupling between y and Y, an exact eigenfunction will not vanish identically in y for any finite Y (This is certainly the case in the coupled oscillator model.). Therefore if the exact θ has nodes at finite Y then the exact ϕ must have compensating poles in Y. However from (1) this is impossible, and therefore θ cannot have such nodes.

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