SOME REMARKS ON THE USE OF THE VARIATIONAL PRINCIPLE FOR THE SECOND ORDER ENERGY*

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ABSTRACT

It is pointed out that if one uses an approximate ground state wave function in the familiar variational principle for the second-order energy, that the approximate energy need have no special relationship to the exact energy (it may be larger or smaller). Further it is shown that in some cases even with full use of the variation principle, good accuracy of the ground state wave function does not imply corresponding accuracy of the approximate energy.

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In situations where one wishes to know a second-order energy correction $E^{(2)}$, but does not have an accurate solution to the zero-order problem, a frequently used technique[1] is to use as an approximation to $E^{(2)}$ the quantity $\tilde{J}$ where

$$\tilde{J} \equiv (\tilde{\Phi}_0, (V-\tilde{E}^{(1)})\tilde{\Psi}^{(1)}) + (\tilde{\Psi}^{(1)}, (V-\tilde{E}^{(1)})\tilde{\Phi}_0) + (\tilde{\Psi}^{(1)}, (H_0-\tilde{E}_0)\tilde{\Psi}^{(1)}) \quad (1)$$

Here $\tilde{\Phi}_0$ is an approximate wave function for the zero-order problem (we will assume throughout that we are dealing with the ground state), H_0 the zero-order Hamiltonian, V the perturbation, $\tilde{E}_0 \equiv (\tilde{\Phi}_0, H_0\tilde{\Phi}_0)$, $\tilde{E}^{(1)} \equiv (\tilde{\Phi}_0, V\tilde{\Phi}_0)$, and $\tilde{\Psi}^{(1)}$ is to be determined variationally from $\delta\tilde{J}=0$.

If we vary $\tilde{\Psi}^{(1)}$ freely (in practice of course one is rarely able to do this) then one is led to a differential equation for the "exact" $\tilde{\Psi}^{(1)}$:

$$(H_0-\tilde{E}_0)\tilde{\Psi}^{(1)} + (V-\tilde{E}^{(1)})\tilde{\Phi}_0 = 0 \quad . \quad (2)$$

We will denote the solution of this equation by $\Psi^{(1)}$ and the value of $\tilde{J}$ to which it leads by J. One then readily finds successively that

$$J = (\tilde{\Phi}_0, (V-\tilde{E}^{(1)})\Psi^{(1)}) = \sum_m (\tilde{\Phi}_0, (V-\tilde{E}^{(1)})\Phi_m)(\Phi_m, \Psi^{(1)}) \quad (3)$$

$$= \sum_m \frac{|(\tilde{\Phi}_0, (V-\tilde{E}^{(1)})\Phi_m)|^2}{\tilde{E}_0 - E_m} \quad (4)$$

where we have introduced the eigen states of H_0: $H_0\Phi_m = E_m\Phi_m$.

Further if we write a general $\tilde{\psi}^{(1)}$ as $\tilde{\psi}^{(1)} = \psi^{(1)} + \delta\psi^{(1)}$ then one has immediately that

$$\tilde{J} - J = (\delta\psi^{(1)}, (H_0 - \tilde{E}_0)\,\delta\psi^{(1)}) \tag{5}$$

From Eq. (2) and (3) we then have the well-known result that if $\tilde{\phi}_0 \equiv \phi_0$ (and hence $\tilde{E}_0 \equiv E_0$) then[2] $J = E^{(2)}$, and Eq. (5) then expresses the well known fact that under these same conditions an arbitrary $\tilde{\psi}^{(1)}$ yields a $\tilde{J}$ which is an upper bound to J and hence to $E^{(2)}$.

In this note we wish to discuss the relationships among J, $\tilde{J}$ and $E^{(2)}$ in the more realistic case $\tilde{\phi}_0 \neq \phi_0$. First, concerning the relationship between J and $\tilde{J}$ it follows immediately from Eq. (5) that J in general is <u>not</u> a lower bound to $\tilde{J}$ since a possible $\delta\psi^{(1)}$ is certainly an arbitrary multiple of ϕ_0. Thus in general $\delta\tilde{J} = 0$ simply yields a stationary point although, of course, if, as is often the case in practice, one is dealing with a $\tilde{\psi}^{(1)}$ of <u>restricted</u> variability, it is quite possible that $\delta\tilde{J} = 0$ may in fact appear to yield a minimum.[3]

We will not attempt a general discussion of the relationship between J and $E^{(2)}$, but instead turn to two simple examples. In each H_0 describes a one-dimensional harmonic oscillator

$$H_0 = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2$$

In example I, $V = x$ while in example II, $V = \frac{1}{2} x^2$. These problems are readily solved exactly and yield, respectively, $E^{(2)} = -1/(2m\omega^3)$ and $-\hbar/(16m^2\omega^3)$

For each example we have evaluated J from equation (4) for $\tilde{\Phi}_0$ given by[4]

$$\tilde{\Phi}_0 = \sqrt{1-\alpha^2}\ \Phi_0 + \alpha \Phi_2$$

The results of the calculation are shown in figures I and II. Let us first discuss example I. Here the important result is that $J \leq E^{(2)}$ not $J \not\geq E^{(2)}$ for the range of α shown (see footnote 4). For other values of α between ± 1 one can get J values arbitrarily larger or smaller than $E^{(2)}$. When coupled with our earlier remarks on the relationship between $\tilde{J}$ and J we have the obvious moral-anything can happen-and we will not belabor the point further.

Now we turn to example II. Here we find $J \not\geq E^{(2)}$ but in a curious way, namely even for $\alpha = 0$, $J \neq E^{(2)}$, and in fact for $\alpha = 0$ we have the largest deviation from $E^{(2)}$. The source of this peculiar behavior is not hard to find; it is in the $n = 0$ term in Eq. (4), which from Eq. (3) can also be written as $(\tilde{\Phi}_0, (V - \tilde{E}^{(1)})\Phi_0)(\Phi_0, \Psi^{(1)})$. For $\alpha = 0$ this term appears as the indeterminant form $0/0$. However if one starts with $\alpha = 0$ initially then, as is well known, Eq. (2) does not determine $(\Phi_0, \Psi^{(1)})$, any finite value is allowed, while on the other hand $(\Phi_0, (V - \tilde{E}^{(1)})\Phi_0) \equiv 0$ whence $0/0$ is to be read as 0, and we have the familiar result for $E^{(2)}$. On the other hand one sees that if one starts with $\alpha \neq 0$ then $(\Phi_0, \Psi^{(1)})$ is determined and in fact is proportional to $1/\alpha$ so that in the limit $\alpha \to 0$ we find that $0/0$ is to be read as a certain finite number. Hence the discrepancy. The moral here then is, in problems for which $(\Phi_0, V\tilde{\Phi}_0)$ and $\tilde{E}^{(1)}$ are not identically zero (they were

identically zero in example I and in most polarizability problems)[5], that even if $\tilde{\Phi}_0$ is very nearly equal to Φ_0, $\tilde{J}$ need not be very close to $E^{(2)}$.

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Figure 1 v = x

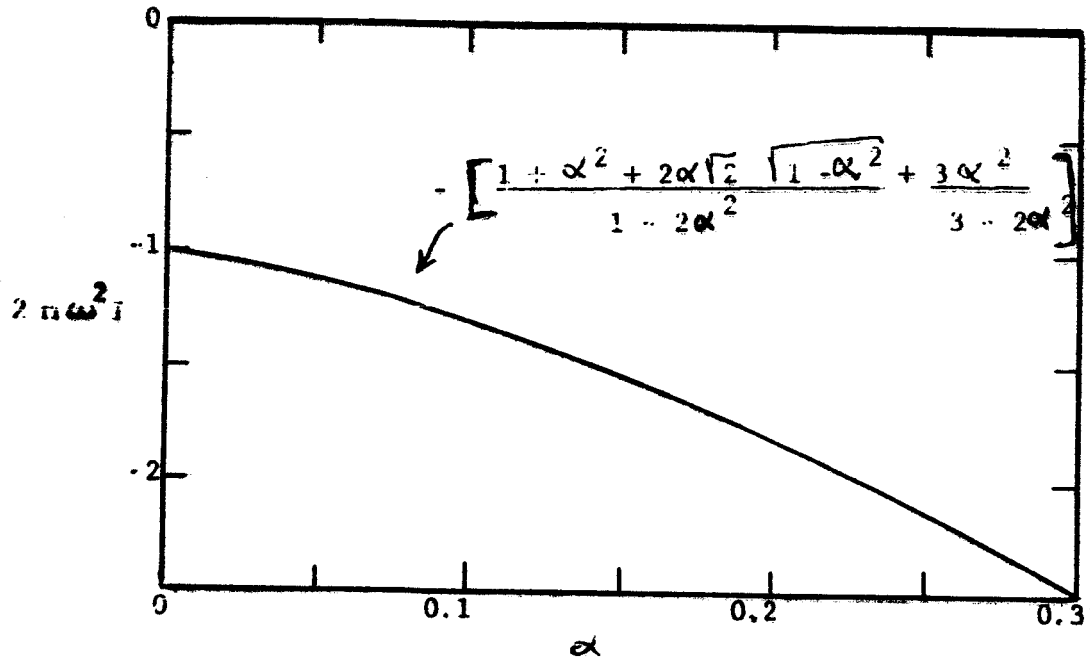
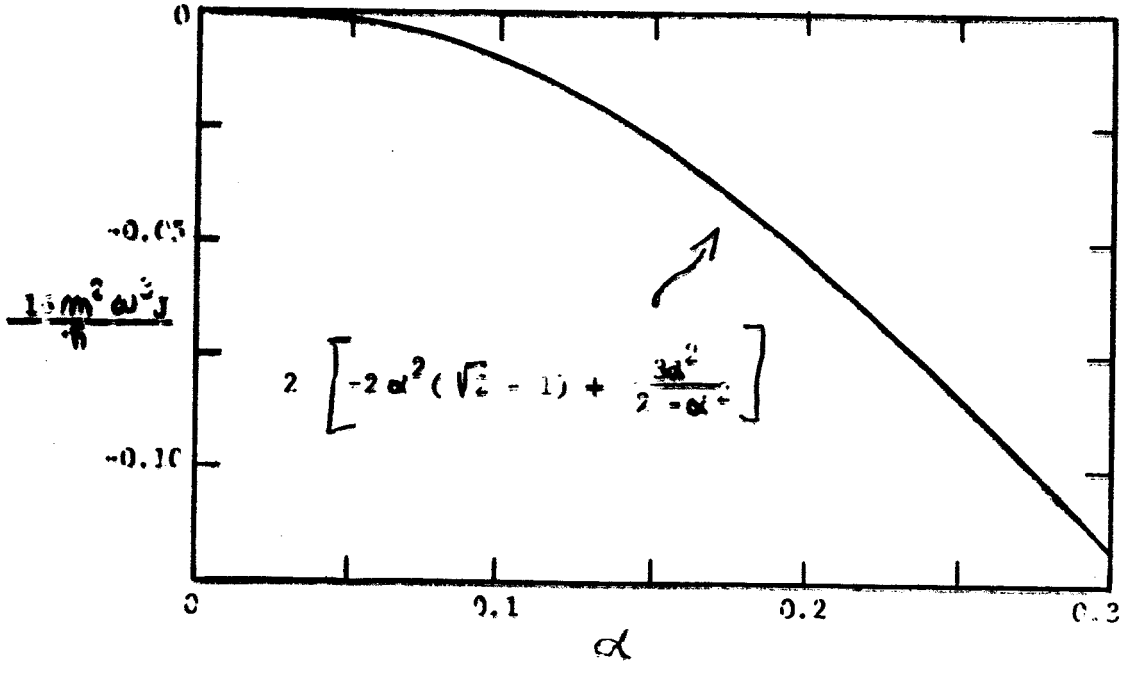


Figure 2: $v = \frac{1}{2} - x^2$



Footnotes and References

1. See for example T. P. Das and R. Bersohn, Phys. Rev., 115, 897 (1959) and M. Karplus and H. J. Kolker, J. Chem, Phys., 38, 1263 (1963). The latter authors also discuss various alternative procedures.
2. We discuss the indeterminate $m=0$ term in Eq. (4) at the end of this note.
3. This is presumably what Das and Bersohn (reference 1) have in mind in the discussion following their Eq. (13) (which is identical to our Eq. (5)).
4. In order that $\tilde{\Phi}_0$ have no nodes and go monotonically to zero as $|x|$ increases, α must be restricted to $0 \leq \alpha \leq \frac{1}{3}\sqrt{\frac{\Sigma}{3}}$ (with the usual definition of the Φ_m).
5. If one redefines $\tilde{E}^{(1)}$ as $\tilde{E}^{(1)} = (\Phi_0, V\tilde{\Phi}_0)$, which also makes $(\Phi_0, \Psi^{(1)}) = 0$, then one gets proper behavior at $\alpha = 0$ and a graph like that of figure I. However this is not a practical way out since by hypothesis we don't know Φ_0 .