Theoret. chim. Acta (Berl.) 4, 343—346 (1966)

Department of Chemistry, University of Illinois, Urbana, Illinois, U.S.A.

# On the Calculation of Energies of Excited States

By

**JERRY GOODISMAN**

We reformulate a scheme for calculation of the energies of excited states which, unlike the variation method, does not require that the trial function be orthogonalized to the wavefunctions for lower excited states. The possibility of obtaining wavefunctions as well as energies is discussed, and an example of the scheme's application is made to the harmonic oscillator.

On donne une nouvelle forme pour une methode de calcul des niveaux excités. La methode ne demande pas l'orthogonalisation de la fonction d'essai par rapport aux fonctions d'onde correspondant aux niveaux inférieurs, ce qui montre un avantage auprès de la methode variationnelle. La possibilité d'obtenir les fonctions d'onde elles-mêmes est discutée, et on donne un exemple de l'application de cette nouvelle methode.

Es wird eine neue Form für eine Methode zur Berechnung von angeregten Zuständen gegeben. Die Probefunktion braucht nicht wie bei der Variationsmethode orthogonal zu den Wellenfunktionen der tiefer liegenden Zuständen zu sein. Es wird die Möglichkeit diskutiert, Wellenfunktionen ebenso wie Energien zu erhalten. Das Schema wird auf den harmonischen Oszillator angewandt.

Except in the case of linear variation functions, the usual variational procedure is of very limited use for excited states. The expectation value of the Hamiltonian is an upper bound for the true excited state eigenvalue only if the trial function is chosen orthogonal to the eigenfunctions corresponding to all lower eigenvalues. While one can often get the *energies* of the ground and perhaps the lower excited states fairly accurately, this by no means implies that one has a good approximation to the true wavefunctions [*1*, *2*, *4*], so the orthogonalization cannot be carried out. We have recently given a scheme [*3*] for obtaining an upper bound to an excited energy level which requires knowledge of the *energy alone* of the state immediately below. Here, we reformulate the method, and discuss the possibility of obtaining eigenfunctions as well as eigenvalues. Throughout, of course, we refer only to states of one fixed symmetry.

The procedure previously presented was the following: a) Choose a trial function for which $\langle H \rangle$, the expectation value of the Hamiltonian, is greater than $E_j$, the $j^{\text{th}}$ eigenenergy. b) Using this function, evaluate $L(\alpha) = \alpha - (\alpha^2 - 2\,\alpha \langle H \rangle + \langle H^2 \rangle)^{\frac{1}{2}}$ as a function of the parameter $\alpha$. c) $L(\alpha)$ is monotomic in $\alpha$. When $L(\alpha) > E_j$, $2\,\alpha - E_j$ will be an upper bound to $E_{j+1}$.

Now $L(\alpha) > E_j$ implies

$$2\,\alpha > (\langle H^2 \rangle - E_j^2)/(\langle H \rangle - E_j)$$

so that

$$2\,\alpha - E_j > (\langle H^2 \rangle - E_j \langle H \rangle)/(\langle H \rangle - E_j)\,.$$

We may show directly that this is not less than $E_{j+1}$ whenever $\langle H\rangle > E_j$, or that

$$\frac{\langle H^2\rangle - E_j\,\langle H\rangle}{\langle H\rangle - E_j} - E_{j+1} \geq 0\,. \tag{1}$$

The left side of (1) may be written as

$$\frac{\langle H^2\rangle - (E_j + E_{j+1})\,\langle H\rangle + E_j\,(E_{j+1})}{\langle H\rangle - E_j}\,.$$

The denominator is positive by hypothesis, while the numerator is equal to the expectation value of $(H - E_j)\,(H - E_{j+1})$. This is a non-negative operator (all eigenvalues $\geq 0$), so its expectation value for any functions is $\geq 0$, and our Theorem is proved.

It is important to point out that nothing may be gained by shifting the zero of energy. If $H \to H + A$, $E_j \to E_j + A$, etc., the left side of (1) becomes

$$\frac{\langle H^2\rangle + A\,\langle H\rangle - E_j\,\langle H\rangle - E_j\,A}{\langle H\rangle - E_j} - (E_{j+1} + A)$$

and all the $A$'s cancel off.

Is it possible, from a consideration of

$$K_j = \frac{\langle H^2\rangle - E_j\,\langle H\rangle}{\langle H\rangle - E_j} \tag{2}$$

alone, to obtain an approximation to the $(j + 1)^{\text{th}}$ eigenfunction as well as the $(j + 1)^{\text{th}}$ eigenvalue? We explore this by writing the trial function $\psi$ as the sum of two parts: the $j^{\text{th}}$ eigenfunction $\psi_j$ and the part orthogonal to $\psi_j$, $X$. If $X$ and $\psi_j$ are taken as normalized to unity,

$$\psi = (\varepsilon^2 + 1)^{-\frac{1}{2}}\,(\varepsilon\psi_j + X) \tag{3}$$

is also normalized. The number $\varepsilon$ is not necessarily small. Now we have

$$\langle H\rangle = (\varepsilon^2 + 1)^{-1}\,(\varepsilon^2\,E_j + \langle X \mid H \mid X\rangle)\,.$$

For this to be greater than $E_j$, we require $\langle X \mid H \mid X\rangle > E_j$. Also,

$$\langle H^2\rangle = (\varepsilon^2 + 1)^{-1}\,(\varepsilon^2\,E_j{}^2 + \langle X \mid H^2 \mid X\rangle)$$

so that

$$K_j = \frac{\langle X \mid H^2 \mid X\rangle - E_j\,\langle X \mid H \mid X\rangle}{\varepsilon^2\,E_j + \langle X \mid H \mid X\rangle - (\varepsilon^2 + 1)\,E_j} = \frac{\langle X \mid H^2 \mid X\rangle - E_j\,\langle X \mid H \mid X\rangle}{\langle X \mid H \mid X\rangle - E_j} \tag{4}$$

i.e. independent of $\varepsilon$.

Eq. (4) expresses both the advantage and shortcoming of the present method. Since $K_j$ does not depend on how much the trial function is contaminated by $\psi_j$, it is clearly not necessary to orthogonalize $\psi$ to $\psi_j$. This also means, however, that one cannot use minimization of $K_j$ to approach the true wavefunction $\psi_{j+1}$, since one would never know how large was the admixture of $\psi_j$ in $\psi$. If $\psi_j$ were known, one could of course orthogonalize $\psi$ to it. For $\langle H\rangle > E_j$, we know that $K_j \geq E_{j+1}$, and if we take $\varepsilon = 0$ and $X = \psi_{j+1}$ in (3) $K_j$ becomes

$$(E_{j+1}^2 - E_j\,E_{j+1})/(E_{j+1} - E_j) = E_{j+1}\,.$$

Then we can use the minimization of $K_j$ to approach $\psi_{j+1}$. The necessity of orthogonalizing $\psi$ to $\psi_j$ brings us almost to the situation we face in variation theory. The advantage still remains that in many cases we need orthogonalize the trial function to one lower eigenfunction only and not to all.

The present scheme for obtaining upper bounds on excited state energies was applied [3] in a different form to the ${}^2\sum_g^+$ states of the molecular ion $H_2^+$. For the first and second excited states, upper bounds were obtained which were, respectively, high by 0.034 and 0.17 atomic units. As a further example, we apply the scheme to the familiar one-dimensional harmonic oscillator problem.

The one-dimensional harmonic oscillator equation

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}\left(E - \tfrac{1}{2}kx^2\right)\psi = 0$$

has the well-known energy levels

$$E_j = \left(j + \tfrac{1}{2}\right)\hbar k^{\frac{1}{2}} m^{-\frac{1}{2}}$$

and the solutions $\psi_j$ are Hermite polynomials times $\exp\left(-\tfrac{1}{2} m^{\frac{1}{2}} k^{\frac{1}{2}} x^2/\hbar\right)$. Let us use a trial function of the form

$$\psi = (2A/\pi)^{\frac{1}{4}} e^{-Ax^2}$$

so that $\psi$ is normalized and

$$-2mH\psi/\hbar^2 = (2A/\pi)^{\frac{1}{4}}\left(-2A + 4A^2x^2 - mkx^2/\hbar^2\right)e^{-Ax^2}.$$

This gives

$$\langle H\rangle = A\hbar^2/2m + k/8A$$

$$\langle H^2\rangle = \frac{\hbar^2}{2m}\left(-\frac{k}{4} + \frac{3A^2\hbar^2}{2m} + \frac{3mk^2}{32A^2\hbar^2}\right).$$

If we now write $A = ak^{\frac{1}{2}} m^{\frac{1}{2}}/\hbar$, so that $a$ is dimensionless, and measure $E_j$ and $E_{j+1}$ in units of $k^{\frac{1}{2}} m^{-\frac{1}{2}}/\hbar$, we have

$$\frac{K_j}{\hbar\sqrt{k/m}} = \frac{48a^4 - 8a^2 + 3 - 32a^3E_j - 8aE_j}{32a^3 + 8a - 64a^2E_j} \geq E_{j+1}. \tag{5}$$

Here, $E_j = (j + 1/2)$ and the condition that $\langle H\rangle$ be greater than $E_j$ is equivalent to having the denominator in (5) positive, so we choose $a$ positive.

The results in the table are what one obtains for $K_j$ with various values of $j$ and $a$. For $j = 0$, any positive $a$ will do, but for $j \neq 0$ the range $E_j - (E_j^2 - \frac{1}{4})^{\frac{1}{2}} \leq a \leq E_j + (E_j^2 - \frac{1}{4})^{\frac{1}{2}}$ is ruled out. We note that the denominator of (5) can be made positive for $a$ large enough, regardless of $j$. This shows the present trial function may be used to get upper bounds on all excited states, although we might consider the trial function as a good approximation for the ground state only. It has no nodes and no maxima for $x \neq 0$, as do the true excited state functions, so does not resemble any of these*. These results are similar to those of Ref. [1]. With the one-parameter trial function, we obtain a good upper bound only for the lowest excited state (2.50 compared to the true value of 1.50). To get comparably good results for other states, we must change the form of the trial function.

---

* I am grateful to Dr. K. Jug for emphasizing this point.

Table. *Calculated Upper Bounds*[a]

| $a$ | $j = 0$ | $j = 1$ | $j = 2$ |
|---|---|---|---|
| 0.01 | 38.5312 | 40.8977 | 43.7375 |
| 0.03 | 13.5491 | 17.0440 | 24.6983 |
| 0.07 | 6.8594 | 22.5830 | — |
| 0.30 | 2.7000 | — | — |
| 0.50 | 2.5000 | — | — |
| 1.00 | 2.8750 | — | — |
| 3.00 | 5.6250 | 103.6250 | — |
| 5.00 | 8.5750 | 14.4774 | 492.5750 |
| 10.00 | 16.0375 | 19.1793 | 24.8136 |

[a] We here give $K_j$, which is an upper bound on $E_{j+1}$. Dashed lines mean denominator of $K_j$ was negative.

## References

[*1*] ECKART, C.: Physic. Rev. **36**, 878 (1930).
[*2*] GOODISMAN, J., and W. KLEMPERER: J. chem. Physics **38**, 721 (1963).
[*3*] — J. chem. Physics **43**, 2806 (1965).
[*4*] LØWDIN, P. O.: Annu. Rev. phys. Chem. **11**, 107 (1960).

*(Received January 31, 1966)*