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Note

A Simplified Shooting Method for the Diatomic Eigenvalue Problem

Among the methods proposed to solve the diatomic vibration–rotation eigenvalue problem, the Cooley shooting method [1] is still the most used by molecular physicists. In his method, Cooley considers the radial Schrödinger equation

$$(d^2/dr^2 + (E - U))\, y(r) = 0, \tag{1}$$

where $U(r)$ is the given potential, r is the internuclear distance, and E is the eigenvalue to be determined under the y boundary conditions

$$y(0) = 0, \qquad y(r) \to 0 \qquad \text{as} \quad r \to \infty \tag{2}$$

For an arbitrary value of the "parameter" E, Cooley starts the integration of Eq. (1) at $r_s \sim 0$ with the initial values $y(r_s) = 0$, $y'(r_s) = c$ (a given constant); he computes $y(r)$ out to an arbitrary point r_m. He then starts at $r_f \sim \infty$ with $y(r_f) = 0$, $y'(r_f) = c$ and integrates Eq. (1) in the opposite direction into r_m. The continuity of $y(r)$ and $y'(r)$ at r_m is obtained by matching $y^+ = y(r_m)$ for $r > r_m$ and $y^- = y(r_m)$ for $r < r_m$, and E is made to vary till the "continuity equation" is satisfied: $y'^+ = y'^-$, where $y'^+ = y'(r_m)$ for $r > r_m$ and $y'^- = y'(r_m)$ for $r < r_m$.

The numerical integration of Eq. (1) is usually done by dividing the r-axis into equally spaced points r_i. Where $r_{i+1} - r_i = h$ is the constant "step-length." In each interval, Eq. (1) is replaced by the Numerov difference equation [2].

The aim of the present work is to propose an alternative to the Cooley shooting method. This alternative is largely inspired from that of Cooley, but it simplifies the procedure. It is based on a simple idea already used for the construction of the potential $U(r)$ from the spectroscopic data by a quantum method [3]. It can be described as follows:

We impose the boundary conditions at $r_s \sim 0$ to y and y'. We use a trial value of E, and we observe the behavior of $y(E; r)$ at the other boundary. By using one of the difference equations, the behavior at $r \sim \infty$ of the computed solution $y(E; r)$ will never be the required exponentially decreasing function approaching the r-axis. y will either: (i) cut the r-axis at a "final" point r_f; (ii) present an extremum at a point that we denote also by r_f and that we call also the "final" point. In a way, r_f can be considered as the numerical "length" of the computed function $y(E; r)$.

In theory, when E is an eigenvalue E^*, r_f must be infinity. When E varies around E^*, r_f varies with E and the representative curve of $r_f = f(E)$ shows an asymptote

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at $E = E^*$. The determination of the eigenvalue E^* is reduced to the accurate "detection" of the asymptote of the curve $r_f = f(E)$.

In practice, one may consider for a given potential $U(r)$, the function $r_f = f(E)$, where the parameter E varies between zero and the dissociation D. The graph $r_f = f(E)$ presents a succession of asymptotes having for abscissas $E_0, E_1, ..., E_n, ...$, the successive eigenvalues related to U.

This approach may be replaced by an equivalent one:

At $r \sim \infty$ the radial Schrödinger equation (1) becomes

$$y'' + (E - D)\, y \simeq 0, \tag{3}$$

where $D = \lim_{r \to \infty} U(r)$. The general solution $y(r)$ behaves, for any E, like

$$y(r) \sim Ae^{-wr} + Be^{wr}, \tag{4}$$

A and B being two constants; w is given by $w^2 = D - E$.

By considering two points in this large r region, say $r_1 = r_f - h$ and $r_2 = r_f$, one may determine A and B in terms of $y_1 = y(r_1)$ and $y_2 = y(r_2)$ and deduce the ratio

$$C = B/A = -(y_1/z_2 - y_2/z_1)/(y_1 z_2 - y_2 z_1), \tag{5}$$

where $z_1 = \exp(wr_1)$ and $z_2 = \exp(wr_2)$.

When we make E to vary, C varies with E. The variation of $C(E)$ versus E (Fig. 1) shows that: (i) this curve presents a succession of asymptotes separated by

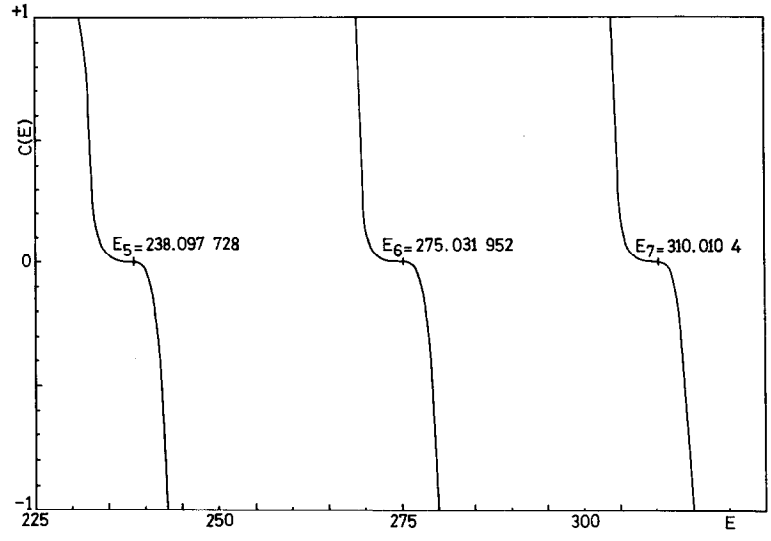

FIG. 1. Variations of $C(E)$ versus E for an interval $225 < E < 325\ \text{cm}^{-1}$. C is computed for the Morse potential defined in the text. The eigenvalues are the abscissas of the intersections of $C(E)$ with the E-axis.

a succession of zeros; (ii) an asymptote corresponds to $C=\infty$, $A=0$, i.e., $y=Be^{wwr}$ (this is the undesired divergent function); (iii) a zero corresponds to $C=0$, $B=0$, i.e., $y=Ae^{-wr}$ (this is the desired convergent function). Thus the zeros $E_0, E_1, E_2, \ldots$ of the function $C(E)$ are the eigenvalues corresponding to the potential $U(r)$.

The determination of the eigenvalues may be obtained either from the function $r_f(E)$ or from the function $C(E)$ defined above. Yet the search of the zeros of $C(E)$ is numerically easier than that of the asymptotes of $r_f(E)$.

For the numerical application, one has to face two problems: (i) The numerical integration of Eq. (1) for a given potential U, and a given trial energy E; (ii) The determination of the zeros of the function $C=f(E)$ when E varies between zero and the dissociation D.

For the first problem, we replace Eq. (1) by the Numerov difference equation (or by any other difference equation). If the function $U(r)$ has no singularity at $r=0$ (like the Morse function [4]), we start at $r_s=0$ by taking $y_0=y(r_s)=0$ and $y_1=y(r_s+h)=c$ (an arbitrary constant for an unnormalized solution), and we step on towards $r\sim\infty$; if $U(r)$ is singular at $r=0$ (like the Lennard–Jones function [5]), we take $r_s\gtrsim 0$. This integration is stopped when $U(r)>E$ and when $y(r)$ cuts the r-axis, or $y(r)$ presents an extremum. In both cases, the two last values of y are used to calculate the function $C(E)$ (Eq. (5)). The problem is then reduced to that of the determination of the zeros of $C(E)$.

Numerically this problem is an easy one. One can realize a first localization of these zeros by making E vary from zero to D and by looking to the intervals $[E_i, E_{i+1}]$ for which we have $C(E_i)\times C(E_{i+1})<0$. Such intervals may contain a zero for $C(E)$ or an asymptote. In order to eliminate the (undesired) asymptote, it is enough to consider $E_m=(E_i+E_{i+1})/2$ and $C(E_m)$. If $C(E_m)$ is greater than $C(E_i)$ and $C(E_{i+1})$ (in absolute values), the interval $[E_i, E_{i+1}]$ contains an asymptote; if not, it contains a zero. The linear shape of $C(E)$ in this interval allows one to use one or another of the conventional techniques to determine the zero of $C(E)$ in the interval.

This procedure was used to compute the eigenvalues for the model Morse function approaching the potential of the Li_2 ground state [6]

$$U(r)=D[1-\exp(-a(r-r_e))]^2,$$

where $a=0.988\,882\,197\,231$ Å^{-1}. $D=605.555$ cm^{-1}, $r_e=2.408\,73$ Å. We give in Table I the eigenvalues computed by the present method (PM) for several values of n up to the highest vibrational level of the potential ($n=23$). Our results are compared to the theoretical Morse eigenvalues E_n^{M} given by [4]

$$E_n^{\mathrm{M}}=w_e(n+1/2)-w_ex_e(n+1/2)^2$$

with $w_e=48.668\,88$, $w_ex_e=0.977\,888$ cm^{-1} [6].

Our results are also compared to those, E_n^{CSM}, obtained by using the Cooley shooting method [7]. In the two applications the same Numerov difference equation is used, with the same constant mesh-size $h=0.001\,375$ Å.

TABLE I

Computed Eigenvalues for the Vibrational Levels of the Morse Potential

n	E^{M}	ΔE^{CSM}	r_f^{CSM}	ΔE^{PM}	r_f^{PM}
0	24.089 968	4.1 (−10)	12	3.4 (−10)	3.7
5	238.097 728	5.4 (−8)	12	5.4 (−8)	4.6
10	403.211 088	2.0 (−7)	12	2.0 (−7)	5.5
15	519.430 048	2.9 (−7)	12	2.9 (−7)	7.0
20	586.754 608	2.0 (−7)	12	2.0 (−7)	10.0
21	594.352 192	1.6 (−7)	12	1.6 (−7)	11.9
22	599.994 000	1.1_4 (−7)	12	1.1_6 (−7)	13.9
23	603.680 032	—	12	6.9 (−8)	18.7

Note. For each level n, the Morse eigenvalue E^{M} is given (in cm^{-1}) along with $\Delta E = E - E^{M}$ for the present method (ΔE^{PM}) and for that of the Cooley shooting method (ΔE^{CSM}). The "numerical length" r_f of the eigenfunction is also given (in Å) for both methods.

We conclude from this comparison that E_n^{PM} and E_n^{CSM} are virtually equal; this result is considered as a confirmation of the validity of the present work.

By looking to the value of r_f obtained for each n (Table I—last column), one can notice its variation with n; while in the conventional shooting method, it is usually predetermined for all the levels ($r_f = 12$ Å). The comparison of r_f^{CSM} (for the Cooley shooting method) and r_f^{PM} (for the present simplified shooting method) leads to the following remarks:

(i) For one "run" (the integration of Eq. (1) for a given E), the CPU time is assumed to be proportional to r_f. The use of the new method requires less time than that of the conventional one for $0 \leqslant n \leqslant 20$.

(ii) The preceding remark is not true for $n > 20$. This is not an advantage for the conventional method, since it fails to obtain E_{23}; the prior guess of r_f being insufficient to reach the appropriate "end point."

(iii) However, this gain in the efficiency does not generate a gain in the accuracy. This fact confirms the assertion of Osborne (and later on of Killingbeck) [8], who noticed that the round-off error in the Cooley shooting method is meaningless, it has no effect on the results.

Similar results are obtained with RKR potentials, and the Lennard–Jones model potential function. This last potential is of particular interest for the present discussion since the Cooley method failed to obtain E_n for the highest levels ($n = 22$ and 23) [9] while the present method does. Even for $n = 23$, the use of the Numerov difference equation gives E_{23} with $\Delta E_{23} = 3 \times 10^{-12}$, the "exact" E_{23} being that given in reference [7]. For this particular application r_f reaches 53 Å. Which is far beyond that ($r_f = 6$ Å) used in the conventional shooting method [9].

Compared to the conventional Cooley method, the present *simplified* shooting method has the following advantages: (i) it avoids the starting problem; (ii) it

shoots in one direction instead of two; (iii) it avoids the "matching" problems used in the Cooley method, and replaces it by the search of the roots of the equation $C(E)=0$; (iv) it does not make any prior guess for r_s and r_f; (v) it reaches the highest levels without any special treatment, even with the Numerov integrator; (vi) it may be used with any integrator.

REFERENCES

1. J. W. COOLEY, *Math. Comput.* **15**, 363 (1961).
2. B. NUMEROV, *Publ. Obs. Central Astrophys. Russ.* **2**, 188 (1933).
3. H. KOBEISSI, *J. Phys. (Paris)* **34**, 235 (1973); H. KOBEISSI AND F. Y. HAJJ, *J. Phys. B* **7**, 1582 (1974).
4. P. M. MORSE, *Phys. Rev.* **34**, 57 (1929).
5. J. E. LENNARD-JONES, *Proc. R. Soc. London Ser. A* **106**, 463 (1924); **107**, 636 (1925).
6. J. K. CASHION, *J. Chem. Phys.* **39**, 1872 (1963).
7. M. DAGHER AND H. KOBEISSI, *J. Comput. Chem.* **9**, 647 (1988).
8. M. R. OSBORNE, *J. Math. Anal. Appl.* **27**, 417 (1969); J. KILLINGBECK, *J. Phys. A* **20**, 1411 (1987).
9. J. M. HUTSON, *J. Phys. B* **14**, 851 (1981); J. TELLINGHUISEN, *J. Mol. Spectrosc.* **122**, 455 (1987).

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