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Note

On the Use of a Variable-Step Method for the Computation of Diatomic Eigenvalues near Dissociation: The Lennard–Jones Potential

In a recent paper [1], Tellinghuisen mentioned some difficulties in the computation of the eigenvalues for the Lennard–Jones potential near dissociation (for $v = 22$ and $v = 23$). The same difficulties were already mentioned by Hutson [2].

In these two works, the method used to compute the eigenvalues, was the widely used *shooting* method described by Cooley [3]. The details of the numerical treatment can be found in Ref. [1].

Another scheme, the *canonical functions approach*, was already presented [4] and applied with equal ease for low and high levels. Examples of the accuracy of the results were given for the eigenvalues of a Morse potential function up to the dissociation [5]. The aim of this note is to explain the causes of the difficulties mentioned above, and to show ways to overcome them.

In a recent paper [6] we applied the canonical functions method to the model Lennard–Jones potential already used by Hutson [2] and by Tellinghuisen [1] ($U(r) = D(1 - r^{-6})^2$ with $D = 10000\ \text{cm}^{-1}$). We found that the range of integration for the highest level ($v = 23$) is quite large: it is limited by $r_{\min} = 0.8$ and $r_{\max} = 73$ Å. This fact was already predicted by Hutson [2] who took $r^H_{\min} = 0.65$ and $r^H_{\max} = 6$ Å for the computation of the eigenvalues up to $v = 20$. It is clear that the total range of integration $\Delta r = r_{\max} - r_{\min}$ is to be multiplied by a factor of 12 in order to treat the highest level. We believe that this is the main cause of the difficulty mentioned above.

The difference equation commonly used in the shooting method is that of Numerov [7]. In the canonical functions method, one may use any difference equation [8]. For both methods, the use of the difference equation with a constant step-size is quite expensive in "computer time" for the two highest levels. In the shooting method the estimated CPU time for $v = 23$ is roughly $12 \times t_{20}$, where t_{20} is the CPU for $v = 20$ (we assume here that t is proportional to Δr, the total range of integration). This remark stands true for the canonical functions method.

For this reason, we tried the recent variable-step difference equation [9]. We give in Table I the computed eigenvalues E_v for several values of v, along with the corresponding values of $r_{\min}$ and $r_{\max}$ effectively used (see below). According to the present method [9], the total number I of the used steps varies from one level to the other. The values of I for the considered levels are given in the last column.

The results of Table I show that the economy in CPU time is impressive. The

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TABLE I

Vibrational Eigenvalues of the Lennard–Jones Potential Computed for Several Levels v by the Canonical Functions Method [4], with the Variable-Step Difference Equation [9]

v	$E(\text{cm}^{-1})$	$r_{\min}$ (Å)	$r_{\max}$ (Å)	I^a
0	589.536 80	0.842 887 69	1.264 455 7	25
4	4521.475 7	0.885 029 93	1.430 885 0	34
8	7205.266 1	0.816 214 52	1.683 869 7	42
12	8847.741 1	0.814 449 68	2.029 649 3	50
16	9681.866 9	0.810 403 03	2.755 923 0	60
20	9969.528 6	0.810 104 48	5.037 244 3	70
21	9989.472 5	0.810 078 64	6.910 158 0	74
22	9998.016 6	0.810 067 36	12.358 140	80
23	9999.973 0	0.810 064 76	73.389 788	94

Note. The highest level is bounded by 2.7×10^{-6} of the well depth. For each v, the inner and the outer numerical limits $r_{\min}$ and $r_{\max}$ are given in angstroms. The last column is reserved for the total number of steps used for each level.

[a] Total number of steps used in the canonical functions scheme [4], between r_e (bottom of the well) and $r_{\max}$, then between r_e and $r_{\min}$.

number of steps given in column 5 shows that this time increases from t_0 (for $v=0$) to approximately $3t_0$ (for $v=20$), and to $4t_0$ (for $v=23$); in other terms $t_{23}=1.3t_{20}$. We deduce from this application that the canonical functions method used with the variable-step difference equation (as presented in Ref. [9]) is highly efficient. We underline that its formulation and the progamming are quite simple; it does not require any sophisticated algorithm nor sophisticated equipment (the present application is done on the personal computer NewBrain AD in eight significant figures).

We finally give an example (for $v=12$) of the determination of $r_{\max}$ (or $r_{\min}$) within the canonical functions scheme. We give in Table II for each step i (each line): (i) the computed variable step-size h_i (starting at the potential minimum $r_e=1$ Å); (ii) the corresponding value of r ($r=r_e+h_1+\cdots$); (iii) the computed ratio $-\alpha(r)/\beta(r)$ where α and β are the two "canonical functions" (starting with $\alpha(r_e)=1$, $\beta(r_e)=0$); (iv) the computed ratio $-\alpha'(r)/\beta'(r)$ (starting with $\alpha'(r_e)=0$, $\beta'(r_e)=1$).

According to the canonical functions method [4], the computation is stopped when the wavefunction ψ_v, and its derivative ψ'_v, approach zero for large r, i.e., $\psi_v(r)=\psi_v(r_e)\,\alpha(r)+\psi'_v(r_e)\,\beta(r)\to_{r\to\infty}0$ and $\psi'_v(r)=\psi_v(r_e)\,\alpha'(r)+\psi'_v(r_e)\,\beta'(r)\to_{r\to\infty}0$. This boundary condition is numerically fulfilled for a value $r_{\max}$, solution of the equation $\lim_{r\to\infty}\alpha/\beta=\lim_{r\to\infty}\alpha'/\beta'$. The example given in Table II shows how this value $r_{\max}$ may be obtained, simply, within any desired precision, and without any prior assumption. The second part of Table II, ($r<r_e$), shows that this work is simply repeated for $r<r_e$ to get $r_{\min}$. (Note that the whole

TABLE II

Variation of the Ratios $-\alpha(r)/\beta(r)$ and $-\alpha'(r)/\beta'(r)$ for $v=12$ ($E_v=0.884774\,114\ \mathrm{cm}^{-1}$) of the Lennard–Jones Potential

Step order i	Step-size h_i	r	$-\alpha/\beta$	$-\alpha'/\beta'$
$r>r_e$				
1	0.017	1.017	4.1889024	−2289.747
2	0.022	1.039	−172.43647	50.68793
3	0.018	1.057	65.03711	−138.73419
4	0.018	1.075	−121.4826	71.552592
5	0.020	1.096	97.714292	−92.818763
6	0.020	1.116	−78.710239	109.78684
7	0.020	1.136	120.75873	−75.59964
8	0.025	1.161	−31.025443	271.0661
9	0.022	1.184	297.79113	−31.605093
10	0.023	1.207	−31.621863	263.26341
11	0.025	1.232	338.55383	−28.393158
12	0.025	1.257	−34.961412	235.98772
13	0.027	1.285	215.6743	−44.192856
14	0.028	1.313	−57.458582	144.07227
15	0.029	1.343	102.49476	−92.976411
16	0.033	1.376	−123.17252	65.752258
17	0.033	1.409	31.714676	−338.3542
18	0.037	1.447	5574.0046	−8.2393134
19	0.038	1.485	−54.056361	131.56203
20	0.041	1.526	41.399893	−365.13348
21	0.045	1.571	235.69303	−80.067024
22	0.047	1.619	−671.94254	−67.451731
23	0.060	1.679	−206.1905	−137.72549
24	0.055	1.734	−176.16384	−167.71689
25	0.052	1.786	−172.59348	−171.76522
26	0.048	1.834	−172.23502	−172.15535
27	0.044	1.879	−172.20017	−172.19221
28	0.041	1.920	−172.19669	−172.19584
29	0.039	1.959	−172.19632	−172.19622
30	0.036	1.995	−172.19627	−172.19626
31	0.034	2.029	−172.19627	−172.19627
32	0.032	2.062	−172.19627	−172.19627

TABLE II—*Continued*

Step order i	Step-size h_i	r	$-\alpha/\beta$	$-\alpha'/\beta'$
$r < r_e$				
1	−0.017	0.983	−4.1729251	2347.3937
2	−0.017	0.966	2509.818	−2.4736377
3	−0.018	0.948	−6.8358459	1934.9313
4	−0.017	0.931	−1102.1259	12.918141
5	−0.016	0.914	47.405603	−141.33843
6	−0.016	0.899	−40.451228	2403.6849
7	−0.014	0.885	−110.22484	−593.64861
8	−0.012	0.873	−155.36869	−202.23166
9	−0.010	0.863	−169.31696	−175.90632
10	−0.009	0.855	−171.79845	−172.66126
11	−0.008	0.847	−172.14518	−172.25368
12	−0.007	0.840	−172.18978	−172.20341
13	−0.006	0.834	−172.19543	−172.19718
14	−0.005	0.828	−172.19616	−172.19639
15	−0.004	0.823	−172.19625	−172.19629
16	−0.003	0.819	−172.19627	−172.19627
17	−0.002	0.814	−172.19627	−172.19627
18	−0.001	0.811	−172.19627	−172.19627

Note. For $r > r_e$, the computation is stopped (and $r_{\max}$ is deduced) when $-\alpha/\beta = -\alpha'/\beta'$. The second part of the table ($r < r_e$) gives $r_{\min}$.

method looks to determine the eigenvalue E_v by imposing the continuity of ψ_v and ψ_v' at r_e, i.e., by imposing the equality: $\lim_{r\to\infty} -\alpha(r)/\beta(r) = \lim_{r\to 0} -\alpha(r)/\beta(r))$.

Other details of the numerical application to the present method may be found elsewhere [9].

We conclude that the "canonical functions variable-step" method is an efficient tool for the diatomic eigenvalue problem near dissociation. It allows the computation of high and low eigenvalues with equal ease.

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