



Fig. 2 Iteration history.

Using the method in Ref. 5, if repeated frequencies meet, another set of design variable values must be given to carry out the iteration. The iteration history (Fig. 2) shows incomplete constraints [constraint Eq. (26) is not taken into account] for cases 1 and 2 in Fig. 2. Case 1 is not converged after 20 iterations; case 2 is converged after 19 iterations. Undoubtedly, the convergence of the Ref. 5 method is associated with the artificial choice of design variable values. For large structures, this method is not feasible.

Using the algorithm presented here the design variable values need not be adjusted artificially, and the iteration is converged stably, i.e., complete constraints [constraint Eq. (26) is taken into account], as shown in Fig. 2. The optimal weight is determined: $W = 1.1610 \times 10^5$ N/m.

V. Conclusion

For large optimal design structures under multiple frequency constraints, especially for symmetric structures that easily exhibit repeated frequencies, using substructural sensitivity synthesis, it is obvious that the computational cost can be decreased and the design period can be shortened. The example demonstrates quick and stable convergence. Hence, the algorithm presented in this Note has good practical value.

Acknowledgment

This work was supported by the National Natural Science Foundation of China under Grant 19472022.

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A. Berman
Associate Editor

Extension of the Rydberg–Klein–Reese Potential for the Nitrogen Molecule

C. Frederick Hansen*

University of Oregon, Eugene, Oregon 97403

Introduction

ONE of the most useful properties of a diatomic molecule is its internuclear potential because all thermodynamic properties of the molecule can be deduced from this potential. For example, the vibration–rotation energies can be determined accurately by integrating the action integral; then the partition function, energy, specific heat, and free energy all follow. In addition, the collision scattering cross sections and the transport coefficients can be determined using the potential.

At low temperatures, where few vibrational levels are excited, useful potentials are obtained by adding quadratic and cubic terms to the usual harmonic oscillator model. However, these expansions fail at high temperature where upper levels are involved. The Morse function¹ has the proper shape near the potential minimum and approaches the correct asymptotic limit, but it is fatter than realistic at intermediate internuclear distances and it vanishes too rapidly at large distances. The most accurate internuclear potential is obtained by the Rydberg–Klein–Reese (RKR) method,^{2,3} where the observed energy levels are used to determine the turning points of vibrational motion at each level. Because spectroscopists can measure energy levels precisely, turning points can be determined accurately. Upper levels become indistinct and so other means must be found to extrapolate RKR potentials beyond the limit of observation. A power series in vibration and rotation quantum numbers can be fit to observed levels with good accuracy, generally within experimental uncertainty. Although these empirical series cannot be extrapolated with great confidence, one can expect that they might retain reasonable accuracy for a few levels beyond the observable threshold at least.

The $X^1\Sigma_g^+$ potential between two ground state ($^4S^0$)N atoms has been studied extensively. The *JANAF Thermochemical Tables*⁴ provide a series of sixth power in vibrational quantum number and quadratic in rotational number that accurately fits observed vibrational levels of ground state N_2 up to the 27th level, roughly half way to the dissociation limit. The RKR potential for ground state N_2 has been reported only to the 21st level.⁵ The RKR potential should be deducible to at least the 27th level using the JANAF representation of vibration–rotation energies because that series accurately predicts energies to that level. Probably the series will retain reasonable accuracy for a number of levels beyond this. It is the purpose of this Note to present this extension of the RKR potential for the nitrogen molecule.

RKR Method

The RKR potential is developed using a function S_v , which is one-fourth the molecule's kinetic energy of motion integrated over one cycle:

$$S_v = \frac{1}{2} \int_{r_1}^{r_2} \left[E_v - V_0(r) - \frac{\kappa}{r^2} \right] dr \quad (1)$$

where E_v is the total vibration rotation energy, r_1 is the minimum and r_2 is the maximum in the internuclear distance r , $V_0(r)$ is the potential function when the rotational quantum number j is zero,

Received March 10, 1997; revision received Oct. 1, 1997; accepted for publication Oct. 6, 1997. Copyright © 1997 by the American Institute of Aeronautics and Astronautics, Inc. All rights reserved.

*Professor, Department of Physics, Chemical Physics Institute. Associate Fellow AIAA.

and the constant κ is $j(j+1)\hbar^2/2\mu$. The functions f and g are defined as derivatives of S_v :

$$f = \left(\frac{\delta S_v}{\delta E_v} \right)_\kappa = \frac{1}{2} \int_{r_1}^{r_2} dr = \frac{r_2 - r_1}{2} \quad (2)$$

$$g = - \left(\frac{\delta S_v}{\delta \kappa} \right)_{E_v} = - \frac{1}{2} \int_{r_1}^{r_2} \frac{dr}{r^2} = \frac{1}{2} \left(\frac{1}{r_1} - \frac{1}{r_2} \right) \quad (3)$$

Then the intersections of the energy E_v with the potential $V_0(r)$ are

$$r_1 = [(f/g^2) + f^2]^{\frac{1}{2}} - f, \quad r_2 = [(f/g^2) + f^2]^{\frac{1}{2}} + f \quad (4)$$

Klein² showed that the integral S_v can be expressed in terms of the vibrational quantum number v :

$$S_v = \left(\frac{2\hbar^2}{\mu} \right)^{\frac{1}{2}} \int_0^{v+\frac{1}{2}} [E_v - V(v, j)]^{\frac{1}{2}} dv \quad (5)$$

where E_v is the constant total vibration-rotation energy of the molecule and the potential $V(v, j)$ is expressed as a function of the vibration and rotation quantum numbers v and j .

Reese³ showed that if the potential is a quadratic in $(v + \frac{1}{2})$ and κ , the integration of Eq. (5) could be performed analytically. Vanderslice et al.⁶ used this method to calculate the RKR turning points for ground state N_2 to the 19th level. Loftus and Krupenie⁵ tabulate slightly improved values to the 21st level. Here the analytic JANAF series for vibration rotation energies is used and integration is performed with a computer. The empirical JANAF series functions⁴ are, in units of the dissociation energy D ,

$$\begin{aligned} E_0 &= 0.0295227(v + \frac{1}{2}) - 1.79445 \times 10^{-4}(v + \frac{1}{2})^2 \\ &\quad - 4.71614 \times 10^{-8}(v + \frac{1}{2})^3 + 3.44678 \times 10^{-9}(v + \frac{1}{2})^4 \\ &\quad - 3.38113 \times 10^{-10}(v + \frac{1}{2})^5 + 2.18932 \times 10^{-12}(v + \frac{1}{2})^6 \\ B &= 2.50117 \times 10^{-4}j(j+1) - 2.16292 \times 10^{-7} \\ &\quad \times (v + \frac{1}{2})j(j+1) - 4.108 \times 10^{-10}(v + \frac{1}{2})^2j(j+1) \\ &\quad - 7.185 \times 10^{-11}j^2(j+1)^2 \\ E &= E_0 + B \end{aligned} \quad (6)$$

Computation of the RKR Potential for $X^1\Sigma_g^+N_2$

With energies expressed in units of the dissociation energy D , the function S , also in units of D , is

$$S(v, j) = \left(\frac{2\hbar^2}{\mu D} \right)^{\frac{1}{2}} \int_0^{v+\frac{1}{2}} [E_v - V(v, j)]^{\frac{1}{2}} dv \quad (7)$$

and the derivatives of S are obtained by numerical differentiation:

$$f = \left(\frac{\delta S}{\delta E_v} \right)_\kappa = \left(\frac{2\hbar^2}{\mu D} \right)^{\frac{1}{2}} \frac{S(v+dv, 0) - S(v-dv, 0)}{E(v+dv, 0) - E(v-dv, 0)} \quad (8)$$

$$g = - \left(\frac{\delta S}{\delta \kappa} \right)_{E_v} = \left(\frac{8\mu D}{\hbar^2} \right)^{\frac{1}{2}} \frac{S(v, 0) - S(v, j)}{j(j+1)} \quad (9)$$

The integrations of S were performed in double precision using 15-point Gaussian quadrature over unit intervals in vibrational quantum number v . The finite intervals dv and j should be very small to obtain accuracy in the derivatives, but if chosen too small roundoff errors can appear in the numerical differentiation. Values of $dv=0.05$ and $j=1$ were found to yield acceptable accuracy. The coefficients required in Eqs. (8) and (9) are for N_2

Table 1 Potential points for vibrational states of $X^1\Sigma_g^+$ of N_2 (internuclear distances r_1 and r_2 , in angstrom)

v	E_v/D	r_1	r_1 (Ref. 5)	r_2	r_2 (Ref. 5)
0	0.01472	1.0552	1.0550	1.1456	1.1456
1	0.04388	1.0267	1.0266	1.1841	1.1843
2	0.07268	1.0085	1.0083	1.2127	1.2130
3	0.10113	0.9944	0.9942	1.2373	1.2377
4	0.12921	0.9827	0.9826	1.2596	1.2600
5	0.15694	0.9726	0.9725	1.2804	1.2809
6	0.18431	0.9637	0.9636	1.3002	1.3007
7	0.21131	0.9555	0.9556	1.3190	1.3197
8	0.23795	0.9483	0.9484	1.3374	1.3382
9	0.26423	0.9416	0.9417	1.3553	1.3561
10	0.29015	0.9355	0.9355	1.3729	1.3738
11	0.31571	0.9298	0.9298	1.3903	1.3911
12	0.34089	0.9245	0.9244	1.4074	1.4082
13	0.36571	0.9196	0.9194	1.4244	1.4252
14	0.39016	0.9149	0.9146	1.4413	1.4420
15	0.41424	0.9105	0.9101	1.4582	1.4588
16	0.43794	0.9063	0.9058	1.4750	1.4755
17	0.46127	0.9023	0.9017	1.4918	1.4921
18	0.48422	0.8985	0.8978	1.5086	1.5088
19	0.50677	0.8947	0.8940	1.5253	1.5255
20	0.52894	0.8912	0.8904	1.5423	1.5423
21	0.55027	0.8878	0.8870	1.5594	1.5591
22	0.57210	0.8846	—	1.5766	—
23	0.59307	0.8815	—	1.5940	—
24	0.61363	0.8784	—	1.6116	—
25	0.63378	0.8755	—	1.6294	—
26	0.65350	0.8726	—	1.6475	—
27	0.67279	0.8696	—	1.6657	—
28	0.69164	0.8668	—	1.6844	—
29	0.71005	0.8641	—	1.7034	—
30	0.72800	0.8614	—	1.7229	—
31	0.74548	0.8585	—	1.7426	—
32	0.76250	0.8558	—	1.7630	—
33	0.77903	0.8531	—	1.7839	—
34	0.79506	0.8502	—	1.8053	—
35	0.81059	0.8474	—	1.8275	—
36	0.82561	0.8445	—	1.8503	—
37	0.84010	0.8415	—	1.8741	—
38	0.85405	0.8384	—	1.8987	—
39	0.86746	0.8352	—	1.9244	—
40	0.88029	0.8318	—	1.9511	—
41	0.89256	0.8283	—	1.9792	—
42	0.90424	0.8245	—	2.0088	—
43	0.91531	0.8205	—	2.0401	—
44	0.92577	0.8162	—	2.0733	—
45	0.93561	0.8115	—	2.1088	—

$$(2\hbar^2/\mu D)^{\frac{1}{2}} = 0.01098155 \text{ \AA}, \quad (8\mu D/\hbar^2)^{\frac{1}{2}} = 364.247 \text{ \AA}^{-1} \quad (10)$$

Results of the computations are shown in Table 1, which gives the turning points of the potential at vibrational levels from 0 to 45. Values reported by Loftus and Krupenie⁵ are shown up to level 21 for comparison. It can be seen that present results generally agree within 0.1%, an indication that the computer program is correct. The small discrepancies could be due to residual error in the Gaussian quadrature or slight deviation of the JANAF series function from measured energy levels.

At levels above $v=27$, the JANAF series can be expected to diverge somewhat from true values, though no doubt it will retain reasonable accuracy to somewhat higher levels. At levels above 35, the calculations indicate a small negative curvature in the repulsive branch of the potential, which is unrealistic. This could be due to a slow drift in the JANAF series away from true energy values at high-quantum levels. The accuracy of the attractive arm of the potential is suspect at these levels also.

Analytic Fit of a Morse-Like Potential to the RKR Results

For some engineering purposes, such as calculating scattering cross sections, it is useful to express the collision potential analytically. The Morse function

$$\begin{aligned}
 U &= D(e^{-2z} - 2e^{-z}) \\
 z &= x + bx^2 + cx^3 + dx^4 + \dots \\
 x &= a(r - r_e)
 \end{aligned}
 \quad (11)$$

can be fit rather precisely to the RKR results if the exponential parameter z is expanded as a series in the dimensionless internuclear distance x . For the $^1\Sigma_g^+$ N_2 state, parameters that fit the known RKR potential⁵ and its extension calculated here from the JANAF vibrational rotation energy levels are

$$\begin{aligned}
 a &= 2.6856 \text{ \AA}^{-1}, & r_e &= 1.094 \text{ \AA}, & D &= 9.9018 \text{ eV} \\
 b &= 0.0437, & c &= 0.0209, & d &= -0.0035
 \end{aligned}
 \quad (11a)$$

The coefficients b and c fit the Morse function of Eq. (11) to the RKR potential reasonably well up to $r = 2.0 \text{ \AA}$. Beyond this point the coefficient d stretches out the Morse function so that the potential will not vanish too rapidly. At long range the potential should vanish inversely as the sixth power of internuclear distance to account for the dispersion forces due to induced polarization by the outer electrons. Partridge et al.⁷ calculated these dispersion forces for N_2 by numerical quantum chemistry methods that should be accurate at large distances, even though their approximations lose accuracy at shorter distances, approaching r_e . The value of d was chosen so that the Morse potential of Eq. (11) will approximate the value and the slope of the leading inverse sixth power term for the dispersion force expression given in Ref. 7:

$$U(r) = -14.048/r^6 \text{ eV}, \quad r > 3.3796 \text{ \AA} \quad (12)$$

The matching potential and slope between Eqs. (11) and (12) occurs at $r = 3.3796 \text{ \AA}$. Therefore, Eq. (11) is the analytic function for the $^1\Sigma_g^+$ N_2 potential for $r < 3.38 \text{ \AA}$ and Eq. (12) is for greater values of r . A simple analytic extension beyond $r = 3.38 \text{ \AA}$ is proposed that provides a realistic asymptotic relation that may be sufficient for some purposes, such as calculating thermodynamic properties⁸ or scattering cross sections with useful engineering accuracy.

Concluding Remarks

The potential for the $X^1\Sigma_g^+$ state of N_2 has been deduced from the JANAF series approximation for the vibration-rotation energies using the RKR method of determining the potential points at these energy eigenvalues. Agreement with the known potential⁵ up to vibrational level 21 indicates that the method used is satisfactorily accurate. Extension to the 27th level, where the JANAF series is known to agree with measurements, is certainly warranted. Beyond this level, the JANAF series may drift away from exact values of vibrational energy. However, discrepancies will presumably be small for some additional states, perhaps up to about the 35th level, where an unrealistic curvature of the repulsive branch of the potential just begins to appear.

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G. M. Faeth
Associate Editor