QTC, NWI-MOL112, computer assignment 2

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Question 1: Morse potential for HF

The Morse potential is given

$$V(r) = \widetilde{D}_e[1 - e^{-\alpha(r-r_e)}]^2, \tag{1}$$

where $\widetilde{D}_e$ is the dissociation energy, r_e is the equilibrium distance, and α is a parameter.

1a. Show that the force constant in the harmonic approximation is given by

$$k \equiv \left.\frac{\partial^2 V(r)}{\partial r^2}\right|_{r=r_e} = 2\widetilde{D}_e\alpha^2.$$

The dissociation energy of HF is $\widetilde{D}_e = 568.6$ kJ/mol. The atomic unit of energy, E_h is 2625.4996 kJ/mol. The spectroscopic constants of the electronic ground state of HF can be found on

http://webbook.nist.gov/chemistry/form-ser.html

Select "Constants of diatomic molecules". The electronic ground state is labeled by X. The rotation-vibration energy levels are represented by so-called term values:

$$E_{v,J} = E_0 + G(v) + F_v(J), \tag{2}$$

for vibrational quantum numbers $v = 0, 1, \ldots$, and rotational quantum numbers $J = 0, 1, \ldots$. The vibrational term values are expanded as

$$G(v) = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 + \omega_e y_e(v + \frac{1}{2})^3 + \ldots \tag{3}$$

and the v-dependent rotational term values as

$$F_v(J) = F_v(0) + B_v J(J+1) - D_v J^2(J+1)^2, \tag{4}$$

where D_v is a rotational distortion constant. Warning: on the NIST website D_v is denoted by D_e, i.e., D_e is not the dissociation energy there! The rotational constant B_v is further expanded as

$$B_v = B_e - \alpha_e(v + \frac{1}{2}), \tag{5}$$

where α_e is a rotation-vibration coupling constant. On the NIST website, all constants are given in wave numbers, $1E_h = 219\,474.63$ cm-1.

The atomic masses are $m_H = 1.007825$ amu and $m_F = 18.998403$ amu. Note that the atomic mass unit (amu) is not an atomic unit! Instead, 1 amu = 1822.8885 m_e, where m_e, the electron mass, is the atomic unit of mass. For convenience, all spectroscopic parameters are listed here:

$$
\begin{aligned}
\omega_e &= 4138.32 \text{ cm}^{-1} \\
\omega_e x_e &= 89.88 \text{ cm}^{-1} \\
\omega_e y_e &= 0.00 \text{ cm}^{-1} \\
\alpha_e &= 0.798 \text{ cm}^{-1} \\
B_e &= 20.9557 \text{ cm}^{-1} \\
D_v &= 0.002151 \text{ cm}^{-1} \\
r_e &= 0.91680 \text{ Å}
\end{aligned}
$$

One Å is 1.8897261 a_0 (atomic unit of length).

1b. Find the parameter α in the Morse potential from the harmonic approximation for k and the relation $\omega_e = \sqrt{k/\mu}$, where μ is the reduced mass of HF.

1c. Compute the first $v_{\max} = 4$ vibrationally excited levels for $J = 0$, using the second order finite difference method. Converge the result with respect to the range of the grid and the grid spacing. Try to converge to three significant digits. Use the analytic expression for the vibrational energies given on Wikipedia to test your program.

1d. Find spectroscopic parameter ω_e, $\omega_e x_e$, and $\omega_e y_e$ from a linear least squares fit to your computed vibrational energies (for $J = 0$). Compare your results to the experimental values (convert parameters to wave numbers).

1e. Compute the rotational terms $F_v(J)$ for $J = 0, 1, \ldots, J_{\max}$, with $J_{\max} = 3$, by adding the centrifugal terms to the potential and repeating the calculation.

1f. Determine B_v and D_v from a linear least squares fit to the computed results, and compare D_v to the experimental value (use wave numbers).

1g. Determine B_e and α_e from a linear least squares fit to the computed B_v's, and again, compare the results to the experimental value.