QTC, NWI-MOL112, exercises week 2

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Question 1: Questions chapter 4

1a. Use first order perturbation theory to show that the energy levels of a diatomic molecule can be written as

$$E_{vl} = \epsilon_v + B_v l(l+1), \tag{1}$$

where $v = 0, 1, 2, \ldots$ is the vibrational quantum number and $l = 0, 1, 2, \ldots$ is the rotational quantum number. Take the vibrational Schrödinger equation with $l = 0$ as the zeroth order problem, and treat the centrifugal term as a perturbation. Assuming that the solutions $\chi_v(r)/r$ of the zeroth-order problem are known, give the expression for B_v.

Reminder first order perturbation theory: Assume the Hamiltonian can be written as

$$\hat{H} = \hat{H}_0 + V \tag{2}$$

and we want to find approximate solutions of

$$\hat{H}\Psi_n = E_n \Psi_n. \tag{3}$$

We assume that the zeroth-order problem has been solved

$$\hat{H}_0 \phi_n = \epsilon_n \phi_n \tag{4}$$

In first order pertubation theory, the energies E_n are given by

$$E_n = \epsilon_n + \frac{\langle \phi_n | V | \phi_n \rangle}{\langle \phi_n | \phi_n \rangle}. \tag{5}$$

A Morse potential has the functional form

$$V(r) = D_e[1 - e^{-\alpha(r - r_e)}]^2 \tag{6}$$

1b. Derive an expression for the vibrational energies ϵ_v, for given parameters D_e, r_e, and α, and assuming the reduced mass of the diatom is μ. To simplify the problem, make an harmonic approximation of the Morse potential, i.e., make a Taylor expansion up to second order around the minimum, and use that as the potential.

1c. Give the expression for B_0 in terms of the Morse parameters and the reduced mass. *Hint: treat the centrifugal term as a perturbation and use the vibrational wave function in the harmonic approximation for $l = 0$. Also, make a linear approximation of the centrifugal term around $r = r_e$.*

1d. Solve the problems that were "left as an exercise" in Chapter 4 of the lecture notes.