

Quantendynamik und Wellenpakete

Sommersemester 2016

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Problem Set No 6

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Problem 6.1 – Rotation scales (6 points)

- (i) Look up on the chemistry webbook.nist.gov the data (“Constants of diatomic molecules”) for the rotational constants of the molecules I_2 , Br_2 , and D_2 (deuterium) in their respective ground states. (You have to choose your favorite isotope, why?) Try to guess a ‘typical rotational period’. Compare the rotational energies for $j = 1, 10$ with the thermal energy at room temperature.
- (ii) Check that the data for the bond length r_e and the rotational constant B are consistent with the classical formula $B = \hbar^2 / (2\mu r_e^2)$.
- (iii) Try to find out the meaning of one of the parameters α_e (“rotational constant, first term”), γ_e (“rotation-vibration interaction constant”), D_e (“centrifugal distortion constant”), β_e (“rotational constant, first term, centrifugal force”). It could well be that they describe the corrections to the vibrational frequency and the rotational constant due to the coupling between the two degrees of freedom. To check this idea qualitatively, compare the numbers you find for these parameters with the ratio $B/\hbar\omega_e$ between the rotational and vibrational constants (read Schödinger’s 1926 paper on Moodle).

Problem 6.2 – Spherical harmonics (8 points)

- (i) In the lecture, we were wondering why the motion of a rotational wave packet was not periodic on the time scale given by the transition $j = 0 \rightarrow 2$. Compute this period T in terms of B and in ps (for I_2). Check that the rotational states $j = 4$ and 10 are not periodic on this time scale. (But they are if the period of the transition $j = 0 \rightarrow 1$ is taken.)
- (ii) Look up the script ‘play_rotation.py’ on Moodle and find a way to present the spherical harmonics $Y_{jm}(\theta, \varphi)$ graphically. A web search related to geographical maps may be useful.
- (iii) Take a superposition of spherical harmonics $Y_{j0}(\theta, \varphi)$ for $j = 8, 10, 12$ and try to construct a ‘wavepacket’ that is localized near the ‘equator’ of the sphere. (Geography convention: identify the z -axis with the South-to-North axis.)

(iv) We have learned in the lecture that the polarisation energy of a diatomic molecule in a laser field is given by

$$V_{\text{pol}} = \text{const} - \frac{\delta\alpha E_z^2(t)}{4} \cos 2\theta \quad (6.1)$$

where $\delta\alpha$ is the difference in polarisabilities and θ the angle between the molecular axis and the z -axis. For the intensity $E_z^2(t)$, we can actually take the time average over one laser period, evaluated at the position of the molecule. (Why?) Take as a typical estimate $\delta\alpha \simeq \varepsilon_0(1 \text{ Bohr})^3$ [check on the web for reliable numbers] and compute for a short pulse the dimensionless number

$$A = \frac{\delta\alpha E_z^2 \tau}{4\hbar} \quad (6.2)$$

that gives the ‘phase modulation depth’ of the rotational wave function. Here, τ is the pulse length. What laser flux is needed to achieve $A \simeq 1$?

(v) The potential (6.1) depends on the orientation of the molecule in such a way that different rotational levels are coupled. Make the expansion

$$\cos 2\theta = aY_{00}(\theta, \varphi) + bY_{20}(\theta, \varphi) \quad (6.3)$$

and look up the ‘addition theorem of spherical harmonics’ to check that

$$\begin{aligned} \langle 0, 0 | \cos 2\theta | 0, 0 \rangle &= -\frac{1}{3} \\ \langle 2, 0 | \cos 2\theta | 0, 0 \rangle &= \frac{4}{\sqrt{45}} \end{aligned} \quad (6.4)$$

all other matrix elements being zero. Here $|j, m\rangle$ is the Dirac notation for $Y_{jm}(\theta, \varphi)$. You can also work out by hand the integrals over Legendre polynomials, of course.

Problem 6.3 – Schrödinger’s diatomic molecule (6 points)

(i) Read in Schrödinger’s 1926 paper (on Moodle) the section on the ‘non-rigid rotator’ and explain in words how he arrived at the equation for the ‘radial wave function $R(r)$ ’ (what is this?)

$$-\frac{\hbar^2}{2\mu} \frac{\partial^2 R}{\partial r^2} + \left[V_g(r) + \frac{\hbar^2 j(j+1)}{2\mu r^2} \right] R = E_{vj} R \quad (6.5)$$

Schrödinger used the harmonic approximation $V_g(r) = \frac{1}{2}\mu\omega_g^2(r - r_g)^2$ for the ground state potential and found an approximate formula for the energy eigenvalues E_{vj} by

expanding the centrifugal potential around r_g up to the second order in $(r - r_g)$. In this way, he finds a j -dependent shift in the bond length and a shifted vibrational frequency. Check that the resulting energy eigenvalues are (attention with notation: $n = j$ (rotation) and $l = v$ (vibration)):

der damaligen Eigenwertbedingung (25) leitet man nun in leichter Rechnung, indem man die Abkürzungen (49), (39') und (39) wieder auflöst und die kleine Größe

$$(50) \quad \varepsilon = \frac{n(n+1)\hbar^2}{16\pi^4\nu_0^2\mu^2r_0^4} = \frac{n(n+1)\hbar^2}{16\pi^4\nu_0^2A^2}$$

als neue Abkürzung einführt, folgende *Energiestufen* ab:

$$(51) \quad \begin{cases} E = E_i + \frac{n(n+1)\hbar^2}{8\pi^2A} \left(1 - \frac{\varepsilon}{1+3\varepsilon}\right) + \frac{2l+1}{2} h\nu_0 \sqrt{1+3\varepsilon} \\ (n = 0, 1, 2, \dots; \quad l = 0, 1, 2, \dots), \end{cases}$$

$A = \text{Trägheitsmoment}$

$\nu_0 = \text{fundamentale Vibrationsfrequenz}$

From here, you can also read off a correction to the rotational constant $B = B(j)$. For the I_2 molecule, compare these predictions to the chemistry webbook data on rotational-vibrational couplings or centrifugal distortion.

(ii) Take the script 'playMorse.py' (on Moodle) and compute numerically the j -dependent shifts of the low-lying vibrational levels for a Morse potential $V_g(r)$. The Morse parameters for the ground state $X^1\Sigma_g^+$ of $^{127}\text{I}_2$ are (webbook)

molecular mass	$2m$	253.80894 amu
vibrational constant	ν_g	214.50 cm^{-1}
anharmonicity	$\nu_g x_e$	0.614 cm^{-1}
bond length	r_g	2.666 Å

(No guarantee that this is an easy numerical task, given the smallness of the ratio $B/h\nu_g$.)