

Quantendynamik und Wellenpakete

Sommersemester 2016

Markus Gühr / Carsten Henkel

Problem Set No 3

Hand out: 12 May 2016

Hand in: 24 May 2016

Problem 3.1 – Aufgabe zu Revivals von Wellenpaketen (10 points)

a) Benutzen Sie das Python-Skript vom ersten Übungszettel, um die Vibrationseigenfunktionen und Energien des B-Zustands (${}^3\Pi_{0u}$) von Jod auszurechnen. (Die letzte Fassung des Skripts liegt mit einer Musterlösung für Aufgabe 1.3 auf moodle.) Die Parameter für die Vibrations-Niveaus in diesem Zustand lauten:

$$\omega_e/2\pi = 125.7 \text{ cm}^{-1} \quad (3.1)$$

$$\omega_e x_e/2\pi = 0.76 \text{ cm}^{-1} \quad (3.2)$$

Ein Jod-Atom hat die Masse $m = 126.9 m_p$.

Am besten rechnen Sie diese Einheiten in atomare Einheiten um, bevor Sie die Schrödinger-Gleichung lösen. Oder Sie skalieren die Schrödinger-Gleichung auf die natürlichen Einheiten, die sich aus der reduzierten Masse μ und der Schwingungsfrequenz ω_e ergeben. Erstellen Sie ein Bildchen mit den Eigenfunktionen, in dem die Achsen in Angström und Wellenzahlen beschriftet sind.

b) Bei welcher Zeit findet ein volles Wellenpaket-Revival statt?

c) Bauen Sie ein Wellenpaket aus den Vibrationseigenfunktionen auf. Die Phase der Eigenfunktionen soll konstant sein. Die Amplitude können Sie gaussförmig als Funktion der Energie wählen. Superponieren Sie mindestens fünf Vibrationseigenzustände. Speichern Sie einen Film des Wellenpakets von der Anregung bis zum vollen Revival in etwa 30 fs Zeitschritten ab.

d) Wählen Sie jetzt eine spektrale Phase, die quadratisch von der Energie abhängt. Ein linear gechirpter Puls würde eine solche Phase unter den Eigenzuständen induzieren. Beobachten Sie, wie das Wellenpaket fokussiert wird. Speichern Sie wieder ein Filmchen dazu.

Problem 3.2 – Anharmonic (Morse) oscillator (10 points)

The Morse potential

$$V(R) = D_e(1 - e^{-a(R-R_e)})^2 \quad (3.3)$$

depends on three parameters: equilibrium position R_e , dissociation limit D_e , and length scale $1/a$.

(i) Expand $V(R)$ around the minimum $R = R_e$ and confirm the following formula involving the oscillation frequency ω_e :

$$a = \sqrt{\frac{\mu}{2D_e}}\omega_e \quad (3.4)$$

where μ is the reduced mass of the molecular oscillator. In addition: check the units, $\mu = m/2$?

(ii) The exact energy levels in this potential can be found [P. M. Morse, “Diatomic molecules according to the wave mechanics. II. Vibrational levels”, *Phys. Rev.* **34** (1929) 57]

$$E_n = \hbar\omega_e(n + \frac{1}{2}) - \hbar\omega_e x_e(n + \frac{1}{2})^2 \quad (3.5)$$

The first term is the ‘harmonic ladder’ of the oscillator. The second term is the first and only anharmonic correction with the dimensionless parameter x_e

$$x_e = \frac{\hbar\omega_e}{4D_e} \quad (3.6)$$

The Morse potential is, of course, just a convenient version of an anharmonic potential. Other potentials would give additional terms in the energy levels E_n , typically featuring higher powers of $n + \frac{1}{2}$. Spectroscopic data show, however, that the additional terms are ‘typically small’.

Question: count the number of discrete states. The largest n appears at the maximum of E_n when plotted as a function of n .

(iii) Classical dynamics: the oscillation frequency in the Morse potential depends on the energy E [N. B. Slater, “Classical motion under a Morse potential”, *Nature* **80** (1957) 1352–53]

$$\nu = \frac{\omega_e}{2\pi} \sqrt{1 - \frac{E}{D_e}}, \quad T = \frac{2\pi}{\sqrt{\omega_e^2 - 4E\omega_e x_e/\hbar}} \quad (3.7)$$

Look up your classical mechanics lecture and derive this formula in the usual way: conservation of energy yields ($v = dR/dt$ is the radial velocity)

$$\frac{\mu v^2}{2} = E - V(R) \quad (3.8)$$

and the period is (*zweimal von innen nach außen*)

$$T = 2 \int_{R_1}^{R_2} \frac{dR}{v(R, E)} \quad (3.9)$$

where R_1 and R_2 are the inner and outer turning points. Slater (1957) gives the hint that the integral can be evaluated with the substitution $y = e^{a(R-R_e)}$.

(iv) Semiclassical quantization: in the Hamilton-Jacobi formulation of classical mechanics, the oscillation period is the derivative of the action

$$T(E) = \frac{\partial S}{\partial E} \quad (3.10)$$

Reverse this formula and compute the action by integrating $T(E)$; an initial value $S(0) = 0$ is reasonable. Now, the semi-classical formula of Bohr and Sommerfeld tells us that the quantized energy levels are those where the action is an integer multiple of $\pi\hbar$:

$$S(E_n) = \pi(n + \frac{1}{2})\pi\hbar \quad (3.11)$$

Check the accuracy of this formula by comparing to the exact spectrum (3.5).

Problem 3.3 – Wigner functions (0 points)

The Wigner function is a way to represent a quantum-mechanical system with the classical position and momentum variables of phase space. We define

$$W(x, p, t) = \int dy e^{-ipy/\hbar} \psi(x + \frac{1}{2}y, t) \psi^*(x - \frac{1}{2}y, t) \quad (3.12)$$

where $\psi(x, t)$ is the wave function. In the following, we shall frequently drop the time argument. There are many different conventions regarding factors $2\pi\hbar$, always check the context.

(i) Use your favorite Fourier transform $\tilde{\psi}(p, t)$ and show that the calculation in momentum space gives the quite symmetrical formula [check signs and the normalization]

$$W(x, p) = \int dq e^{iqx/\hbar} \tilde{\psi}(p + \frac{1}{2}q, t) \tilde{\psi}^*(p - \frac{1}{2}q, t) \quad (3.13)$$

(ii) Check the normalization of the Wigner function

$$1 = \int \frac{dx dp}{2\pi\hbar} W(x, p, t) = \int dx |\psi(x, t)|^2 \quad (3.14)$$

This motivates the analogy to classical mechanics: we may think of a ‘cloud of point particles’ in phase space, and W plays a similar role as the distribution function of kinetic theory. We shall see, however, that in some cases, $W(x, p, t)$ can be negative so that an interpretation as a classical probability fails.

(iii) The overlap between two wave functions $\psi_{1,2}$ is given by [check factors]

$$|\langle \psi_1 | \psi_2 \rangle|^2 = \int \frac{dx dp}{2\pi\hbar} W_1(x, p) W_2(x, p) \quad (3.15)$$

We shall see in the lecture that a gaussian wave packet has a positive and gaussian Wigner function. Since the lhs of Eq.(3.15) is positive, the ‘negative regions’ of the Wigner function cannot be ‘too big’: once W_1 is integrated over a gaussian wavepacket (minimum uncertainty area $\mathcal{O}(\hbar)$ in phase space), the result is positive (well, non-negative for the mathematician).

(iv) The position and momentum distributions of the wavepacket are given by the ‘projections onto the x - and p -axes’ [check factors]

$$|\psi(x)|^2 = \int \frac{dp}{2\pi\hbar} W(x, p) \quad (3.16)$$

$$|\tilde{\psi}(p)|^2 = \int \frac{dx}{\hbar} W(x, p) \quad (3.17)$$

Make a sketch for an excited state of the harmonic oscillator where $|\psi_n(x)|^2$ oscillates. Look up the Wigner function on the web: you will find that $W(x, p)$ for this state depends only on the energy $H(x, p)$.

(v) Finally, the probability current can be written like in kinetic theory

$$j(x) = \frac{\hbar}{m} \text{Im} \left[\psi^*(x) \frac{d\psi}{dx} \right] = \int \frac{dp}{2\pi\hbar} \frac{p}{m} W(x, p) \quad (3.18)$$