Makroskopische Quantenzustände und kalte Gase

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Problem 0.1 – Electric dipole matrix elements (10 points)

For atoms with a single outer-shell electron, the electric dipole operator is directly proportional to the coordinate $\mathbf{r}$ of that electron

$$\mathbf{d} = e\mathbf{r} \tag{0.1}$$

(1) Find a symmetry argument that in a stationary orbital with quantum numbers n, l, m, s (s: spin projection), there is no average dipole moment.

(2) Look up the hydrogen-like wave functions of single-electron atoms and write down the overlap integrals corresponding to

$$\langle 2\mathrm{p}_z | d_z | 1\mathrm{s} \rangle \,, \qquad \langle 2\mathrm{p}_z | d_x | 1\mathrm{s} \rangle \,, \qquad \langle 2\mathrm{s} | d_z | 1\mathrm{s} \rangle \tag{0.2}$$

Show that the last two are zero.

(3) In hydrogen, the matrix elements can be computed analytically from the Laguerre polynomials. Two results are

$$\langle 2\mathrm{p}_z | d_z | 1\mathrm{s} \rangle = \frac{128\sqrt{2}}{243} e a_0 \,, \qquad \langle 2\mathrm{p}_1 | (d_x + \mathrm{i} d_y) | 1\mathrm{s} \rangle = -\frac{256}{243} e a_0 \tag{0.3}$$

(no guarantee for signs). Check these values for consistency with the decay rates (radiative life times) of the $2\mathrm{p}$ states. They are given by

$$\gamma_{2\mathrm{p}m} = \frac{\omega_{21}^3}{3\pi\varepsilon_0 \hbar c^3} |\langle 2\mathrm{p}m | \mathbf{d} | 1\mathrm{s} \rangle|^2 \tag{0.4}$$

where $\hbar\omega_{21} = E_2 - E_1$ is the Lyman-α frequency.

(4) How would Eq.(0.1) be generalised to atoms with more than one electron?

Problem 0.2 – Sum rule (10 points)

The electric dipole matrix elements are also useful for the minimal coupling scheme where the relevant interaction with light is

$$V = -\frac{e}{2m} \{\mathbf{p} \cdot \mathbf{A}(\mathbf{r}) + \mathbf{A}(\mathbf{r}) \cdot \mathbf{p}\} \tag{0.5}$$

(1) Interpret the quantities in this formula.

(2) Show from the Heisenberg equations of motion

$$\frac{d\mathbf{r}}{dt} = \frac{\mathrm{i}}{\hbar}\,[H, \mathbf{r}] \tag{0.6}$$

that the matrix elements of the momentum and position operators are related by

$$\langle n'|\mathbf{p}|n\rangle = \frac{\mathrm{i}m}{\hbar}\langle n'|\,[H_0, \mathbf{r}]\,|n\rangle = \mathrm{i}m\omega_{n'n}\langle n'|\mathbf{r}|n\rangle \tag{0.7}$$

where H_0 is the atom Hamiltonian without the coupling to the electromagnetic field (but including the Coulomb potential of the nucleus!).

(3) We continue this game by evaluating the matrix elements of the commutator

$$[r_k, p_l] = \mathrm{i}\hbar\delta_{kl} \tag{0.8}$$

The upshot is the so-called Thomas–Reiche–Kuhn sum rule

$$\frac{1}{2}\sum_{n'} \omega_{n'n}\left\{\langle n|d_i|n'\rangle\langle n'|d_j|n\rangle + \langle n|d_j|n'\rangle\langle n'|d_i|n\rangle\right\} = \frac{\hbar}{2}\delta_{ij}\sum_{\alpha}\frac{e^2}{m} \tag{0.9}$$

where $n = \{n, l, \ldots\}$ and n' are sets of quantum numbers and the summation actually includes contributions from the continuum, too. The sum on the right is proportional to the total number of electrons in the atom.

(4) The oscillator strength of a given transition $n \to n'$ is defined as

$$f_{nn'} = \frac{2m}{e\hbar}\omega_{n'n}|\langle n'|\mathbf{d}|n\rangle|^2 \tag{0.10}$$

Using the Thomas–Reiche–Kuhn sum rule, show that the oscillator strengths sum up to unity: $\sum_{n'} f_{nn'} = 1$, aka the f-sum rule.

(5) The alkali atoms have very strong transitions (the D lines) whose oscillator strength nearly 'saturates' this sum rule. Look up the D lines of some alkali atom and compare its oscillator strength to unity. One way would be to check the radiative linewidth, Eq.(0.4). A useful resource is NIST's Atomic Spectra Database. A citation from the 'Basic Handbook':

> **A. Transition probabilities**
>
> The values are listed as A_{ki} in units of $10^8\mathrm{s}^{-1}$. These A_{ki} values can easily be converted to oscillator strengths, f_{ik}, $g_i f_{ik}$, or $\log(g_i f_{ik})$, or line strength, S, by using the following formula:
>
> $$g_i f_{ik} = 1.499 \times 10^{-8} A_{ki}\lambda^2 g_k = 303.8\lambda^{-1}S\,,$$
>
> where i refers to the lower energy level, k refers to the upper level, λ is the wavelength in Ångstroms, and $g = 2J + 1$ for a given level.

So what is the physical meaning of A_{ki}?

Problem 0.3 – Do it yourself: problems to come (10 points)

Python. Evaluate Laguerre polynomials, spherical harmonics. Compute dipole matrix elements. Next step: solve Schrödinger equation.