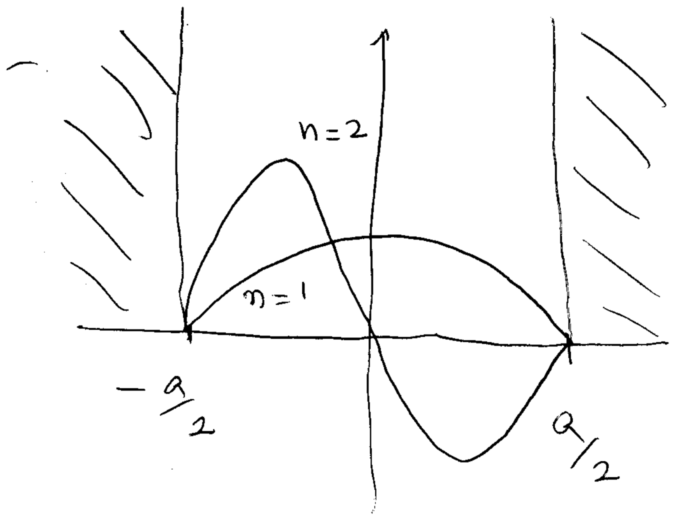
Exercises

1. An electron is confined to the region $-\frac{a}{2} \leq x \leq \frac{a}{2}$ by an infinitely deep one-dimensional square well potential.

The normalized wavefunctions for the electron are

$$\psi_n(x) = \left(\frac{2}{a}\right)^{1/2} \sin\left[\frac{n\pi(x+a/2)}{a}\right], \text{ with } n = 1, 2, 3, \dots \infty$$



(a) Show that the matrix elements of the electric dipole operator $D = ex$, taken between states of quantum numbers n_1 and n_2 are given by

$$D_{n_1,n_2} = \frac{ea}{\pi^2}\left[\frac{\cos[(n_1-n_2)\pi]-1}{(n_1-n_2)^2} - \frac{\cos[(n_1+n_2)\pi]-1}{(n_1+n_2)^2}\right]$$

Matrix element of dipole operator:

$$D_{n_1,n_2} = \int_{-a/2}^{a/2} \psi^*_{n_1}(x)\, D\, \psi_{n_2}(x)\, dx$$

$$= \int_{-a/2}^{a/2} e\,x \left(\frac{2}{a}\right) \sin\left[\frac{n_1\pi(x+a/2)}{a}\right] \sin\left[\frac{n_2\pi(x+a/2)}{a}\right] dx$$

Shift $\tilde{x} = x + a/2$; $x = \tilde{x} - \frac{a}{2}$

$$D_{n_1,n_2} = \int_0^a e\left(\frac{2}{a}\right)\left(\tilde{x}-\frac{a}{2}\right) \sin\left(\frac{n_1\pi\tilde{x}}{a}\right) \sin\left(\frac{n_2\pi\tilde{x}}{a}\right) d\tilde{x}$$

$$= \frac{e}{a}\Bigg[\overbrace{\frac{1}{2}\int_0^a x \left\{\left[\cos\left(\frac{(n_1-n_2)}{a}\pi x\right)\right] - \cos\left[\frac{(n_1+n_2)}{a}\pi x\right]\right\} dx}^{I_1} +$$

$$\underbrace{- \frac{a}{4}\int_0^a \left\{\cos\left[\frac{(n_1-n_2)\pi x}{a}\right] - \cos\left[\frac{(n_1+n_2)\pi x}{a}\right]\right\} dx}_{I_2}\Bigg]$$

$$I_2 = \frac{a}{4}\int_0^a \cos\left[\frac{(n_1 \pm n_2)\pi x}{a}\right] = \frac{a}{4} \cdot \frac{a}{(n_1 \pm n_2)\pi} \sin\left[\frac{(n_1 \pm n_2)\pi x}{a}\right]\Bigg|_0^a$$

$$I_2 = 0$$

I_1 (by parts) :

$$I_1 = \frac{x\,a}{(n_1-n_2)\pi} \underbrace{\sin\left[\frac{(n_1-n_2)\pi x}{a}\right]}_{\substack{\| \\ 0}}\Bigg|_0^a + \frac{x\,a}{(n_1+n_2)\pi} \underbrace{\sin\left[\frac{(n_1+n_2)\pi x}{a}\right]}_{\substack{\| \\ 0}}$$

$\sin(n_1 \pm n_2)\pi = 0$

$\sin 0 = 0$

$$-\left[\frac{a}{(n_1-n_2)\pi}\int_0^a \sin\left[\frac{(n_1-n_2)\pi x}{a}\right]dx - \frac{a}{(n_1+n_2)\pi} \times \int_0^a \sin\left[\frac{(n_1+n_2)\pi x}{a}\right]dx\right]$$

$$\int_0^a \sin\left[\frac{(n_1 \pm n_2)\pi x}{a}\right]dx = -\frac{a}{(n_1 \pm n_2)\pi}\cos\left(\frac{[n_1 \pm n_2]\pi x}{a}\right)\Bigg|_0^a$$

$$\Rightarrow I_1 = \frac{a^2}{\pi^2}\left[\frac{\cos[(n_1-n_2)\pi]-1}{(n_1-n_2)^2} - \frac{[\cos[(n_1+n_2)\pi]-1]}{(n_1+n_2)^2}\right]$$

$$\Rightarrow D_{n_1 n_2} = \frac{e\,a}{\pi^2}\left[\frac{\cos[(n_1-n_2)\pi]-1}{(n_1-n_2)^2} - \frac{\cos[(n_1+n_2)\pi]-}{(n_1+n_2)^2}\right.$$

(b) Based on the previous results, could you derive selection rules for a one-photon electric dipole transition from state n_1 to state n_2?

According to the above-stated expression,

D_{n_1, n_2} is non-vanishing if

$\cos[(n_1 \pm n_2)\pi] - 1 \neq 0$. Hence $n_1 \pm n_2$ odd

$\Rightarrow$ If n_1 odd, n_2 even
If n_1 even, n_2 odd

(c) Could you reach the same conclusions without computing D_{n_1, n_2} explicitly?

Yes. An electric dipole transition couples levels of different parities

$n = 1 \Rightarrow \psi_n$ even
$n = 2 \Rightarrow \psi_n$ odd
$n = 3 \Rightarrow \psi_n$ even
⋮

Hence, a dipole transition can only couple n_1 odd to n_2 even or vice-versa.

(*) Moral of the story:

- Selection rules involving quantum numbers will depend on the bound-state wavefunctions - may be approximate if ψ is not exact
- Selection rules based on the parity are much stronger

(2) Assuming L-S coupling determine the terms which arise from the following electron configurations

(a) He $(2p^2)$

$$\left.\begin{array}{l} l_1 = 1 \\ l_2 = 1 \end{array}\right\} L = 0, 1, 2 \quad (\text{from } l_1 - l_2 \text{ to } l_1 + l_2)$$

$$\left.\begin{array}{l} s_1 = +1/2 \\ s_2 = -1/2 \end{array}\right\} S = 0, 1$$

terms take the form ^{2S+1}L

$S = 0$, $2S+1 \rightarrow 1$ "singlet" $\quad {}^1S \quad {}^1P \quad {}^1D$

$S = 1$, $2S+1 \rightarrow 3$ "triplet" $\quad {}^3S \quad {}^3P \quad {}^3D$

The electrons are equivalent and therefore the whole wavefunction must be antisymmetric.

Spatial wavefunction: Parity $(-1)^l$ $\quad S = \text{even}$, $P = \text{odd}$, $D = \text{even}$

Spin wavefunction: triplet → symmetric
singlet → antisymmetric

$|\psi\rangle = |\psi_e\rangle \otimes |\psi_s\rangle$ antisymmetric

$^1S \rightarrow$ antisymmetric ✓
$^1P \rightarrow$ symmetric ✗ cannot exist

$^1D \to$ antisymmetric ✓

$^3S \to$ symmetric ✗

$^3D \to$ symmetric ✗

$^3P \to$ antisymmetric ✓

^1S, ^1D and ^3P

(b) He $(2p2s)$

The electrons are non-equivalent

$l_1 = \cancel{1}$

$l_2 = 0$

$L = 1$

$s_1 = 1/2$

$s_2 = 1/2$

$S = 0, 1 \to$ singlets and triplets

$\Rightarrow$ ^1P ^3P