Universidad Complutense de Madrid
Departamento de Física Teórica I

Mecánica cuántica avanzada - Problemas resueltos (Licenciatura en Física, 4º curso)

PROBLEMA. Un átomo de hidrógeno se ve sometido a una perturbación

$$V = \begin{cases} 0 & t < 0 \\ f(r)\, \boldsymbol{a} \cdot \mathbf{P} & t \geq 0 \end{cases} ,$$

donde $r = |\mathbf{x}|$ es la distancia radial, $f(r)$ es una función que depende sólamente de r y $\boldsymbol{a}$ es un vector constante conocido.

(i) Calcular las reglas de selección para el momento angular en la aproximación de Born para la transición $|n, \ell, m\rangle \to |n', \ell', m'\rangle$.

(ii) ¿Es posible a este orden en teoría de perturbaciones una transición entre estados con el mismo número cuántico n? Razonar la respuesta. En caso de serlo, calcular la probabilidad de transición en un tiempo T para $n = n' = 2$ y $\ell = 0$ y una función

$$f(r) = \frac{f_0}{r} \quad r > 0 ,$$

con f_0 una constante de dimensiones adecuadas.

SOLUCIÓN (expresiones finales en rojo).

The transition probability in Born's approximation is given by

$$P := P^{(\mathrm{B})}_{i\to f}(0,T) = \left| \frac{1}{\hbar} \int_0^T dt\; e^{\omega_{fi} t}\, V_{fi} \right|^2 ,$$

where

$$|i\rangle = |\, n_i\, \ell_i\, m_i\,\rangle , \qquad |f\rangle = |\, n_f\, \ell_f\, m_f\rangle ,$$

$$\omega_{fi} = \frac{E_f - E_i}{\hbar} = \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \frac{m\,(Z\alpha c)^2}{2\hbar} ,$$

$$V_{fi} = \langle f|\, f(r)\, \mathbf{a}{\cdot}\mathbf{P}\, |i\rangle = \sum_{j=1}^{3} a^j\, \langle f|\, f(r)\, P^j\, |i\rangle .$$

Taking into account that V_{fi} does not depend on t and noting

$$F_{fi}(T) := \left| \int_0^T dt\ e^{\mathrm{i}\omega_{fi} t} \right|^2 = \begin{cases} T^2 & \text{if} \quad n_i = n_f \\ \dfrac{\sin^2\left(\frac{\omega_{fi} T}{2}\right)}{\left(\frac{\omega_{fi} T}{2}\right)^2} & \text{if} \quad n_i \neq n_f \end{cases},$$

it follows that

$$P = F_{fi}(T)\, |V_{fi}|^2 .$$

(i) The selection rules are those for V_{fi}. Being $f(r)$ a scalar and $\mathbf{P}$ a vector, the perturbation operator V has $\ell = 1$. The selection rules for the angular momentum are then

$$\ell_f - \ell_i = -1, 0, 1 \quad \text{and} \quad \ell_f = 1 \ \text{ if } \ \ell_f = 0.$$

Since $\mathbf{P}$ is odd, the state $|n, \ell, m\rangle$ must change its parity. Hence

$$\ell_f - \ell_i = -1, 1 \quad \text{and} \quad \ell_f = 1 \ \text{ if } \ \ell_f = 0.$$

(ii) The Hamiltonian for the Hydrogen atom is

$$H_0 = \frac{\mathbf{P}^2}{2m} + \frac{Ze^2}{|\mathbf{x}|} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{\mathbf{L}^2}{r^2} \right) + \frac{Ze^2}{r} .$$

Using $[X^j, H_0] = \dfrac{\mathrm{i}\hbar}{m} P^j$ we write V_{fi} as

$$V_{fi} = \frac{m}{i\hbar} \sum_{j=1}^{3} a^j \, \langle f|\, f(r) \left(x^j H_0 - H_0\, x^j \right) |i\rangle \, . \tag{1}$$

The first term in this expression is straightforward,

$$\sum_{j=1}^{3} a^j \, \langle f|\, f(r)\, x^j H_0 \,|i\rangle = E_i \, \langle f|\, f(r)\, \mathbf{a}\cdot\mathbf{x}\, |i\rangle \, . \tag{2}$$

As regards the second one, note that H_0 cannot be pulled to the left to act on $\langle f|$ since $f(r)$ is on the way. To reach $\langle f|$, H_0 must first commute with $f(r)$,

$$f(r)\, H_0 = [f(r)\, , H_0] + H_0\, f(r)\, .$$

This and

$$[H_0\, , f(r)] = -\frac{\hbar^2}{2m} \left[f''(r) + \frac{2}{r}\, f'(r) + 2\, f'(r)\, \frac{\partial}{\partial r} \right]$$

imply that

$$\sum_{j=1}^{3} a^j \, \langle f\,|\, f(r)\, H_0\, x^j \,|i\rangle = \frac{\hbar^2}{2m} \left\langle f \left| \left(f'' + \frac{2}{r}\, f' + 2\, f'\, \frac{\partial}{\partial r} \right) \mathbf{a}\cdot\mathbf{x} \right| i \right\rangle + E_f\, \langle f\,|\, f(r)\, \mathbf{a}\cdot\mathbf{x}\,|i\rangle \, . \tag{3}$$

Substituting (2) and (3) in (1), recalling that the bound states $|n\ell m\rangle = |n\ell\rangle\,|\ell m\rangle$ for the Hydrogen atom have wave functions $\psi(r,\theta,\phi) = R_{n\ell}(r)\,Y_\ell^m(\theta,\phi)$, employing

$$\mathbf{a}\cdot\mathbf{x} = r\,\frac{\mathbf{a}\cdot\mathbf{x}}{r}$$

and noting that $\mathbf{a}\cdot\mathbf{x}/r$ does not depend on r, we obtain

$$V_{fi} = i\,\mathcal{R}_{fi}\,\mathcal{A}_{fi}\,,$$

where $\mathcal{R}_{fi}$ and $\mathcal{A}_{fi}$ stand for the radial and angular contributions,

$$\mathcal{R}_{fi} = \frac{m}{\hbar}\,(E_f - E_i)\,\langle n_f\,\ell_f|\,f(r)\,|n_i\,\ell_i\rangle + \frac{\hbar}{2}\,\Big\langle n_f\,\ell_f\Big|\Big(r f'' + 4f' + 2r f'\,\frac{d}{dr}\Big)\Big|n_i\,\ell_i\Big\rangle\,,$$

$$\mathcal{A}_{fi} = \Big\langle \ell_f\,m_f\,\Big|\,\frac{\mathbf{a}\cdot\mathbf{x}}{r}\,\Big|\,\ell_i\,m_i\Big\rangle\,.$$

Let us look at the radial contribution $\mathcal{R}_{fi}$ for $n_f = n_i$. In this case the difference $E_f - E_i$ vanishes and the first term in $\mathcal{R}_{fi}$ is zero, so that

$$\mathcal{R}_{fi} = \frac{\hbar}{2}\,\Big\langle n\,\ell_f\Big|\Big(r f'' + 4f' + 2r f'\,\frac{d}{dr}\Big)\Big|n\,\ell_i\Big\rangle, \qquad n = n_f = n_i\,.$$

This is in general different from zero, hence transitions $i \to f$ with $n_f = n_i$ are allowed. Take $n_i = n_f = 2$, $\ell_i = 0$ and $f(r) = f_0/r$. In this case the only possible value for ℓ_f is 1 and

$$\mathcal{R}_{fi} = -\hbar\,f_0\,\Big\langle 2\,1\Big|\Big(\frac{1}{r^2} + \frac{1}{r}\,\frac{d}{dr}\Big)\Big|2\,0\Big\rangle\,.$$

We recall that

$$R_{20}(r) = \frac{1}{\sqrt{2}\,a_0^{3/2}}\,\Big(1 - \frac{r}{2a_0}\Big)\,e^{-r/2a_0}\,,\quad R_{21}(r) = \frac{1}{2\sqrt{6}\,a_0^{3/2}}\,\frac{r}{a_0}\,e^{-r/2a_0}\,,$$

where a_0 is Bohr's radius. Some integration then gives

$$\mathcal{R}_{fi} = \frac{\hbar f_0}{12\,a_0^2}\,.$$

The angular part $\mathcal{A}_{fi}$ reproduces the selection rules already found. To compute it, we choose the Oz axis in the integral parallel to the direction defined by the vector $\mathbf{a}$, so that

$$\mathcal{A}_{fi} = a\int d\Omega\;Y_{\ell_f}^{m_f\,*}(\theta,\phi)\;\cos\theta\;Y_{\ell_i}^{m_i}(\theta,\phi) = \sqrt{\frac{4\pi}{3}}\;a\;\underbrace{\langle\,Y_{\ell_f}^{m_f}\,|\,Y_1^0\,|Y_{\ell_i}^{m_i}\,\rangle}_{\text{Clebsch-Gordan coeff}}.$$

where we have used that

$$\cos\theta = \sqrt{\frac{4\pi}{3}}\;Y_1^0$$

The matrix element in blue is the Clebsch-Gordan coefficient $\langle \ell_f\, m_f | 1\, 0\, ; \ell_i\, m_i\rangle$. For $n_i = n_f = 2$, $\ell_i = 0$, which in turn implies $\ell_f = 1$, $m_i = m_f = 0$. It is clear that

$$\mathcal{A}_{fi} = \frac{a}{\sqrt{3}}\,.$$

Putting everything together, the probability becomes

$$P(2s \to 2p) = \frac{\hbar^2\, f_0^2\, |\mathbf{a}|^2}{2^4\, 3^3\, a_0^4}\; T^2\,.$$

This is only valid for T such that $P \ll 1$.

Comment. The expression of $\mathcal{R}_{fi}$ can be further elaborated. To this end recall that

$$R_{n\ell}(r) = C_{n\ell}\;\, e^{\rho/2}\, \rho^\ell\, L^{2\ell+1}_{n-\ell-1}(\rho)\,,$$

where $L^\alpha_k(\rho)$ are the generalized Laguerre polynomials and the constant $C_{n\ell}$ and the dimensionless variable ρ are given by

$$C_{n\ell} = \frac{2}{n^2 a_0^{3/2}} \left[\frac{(n-\ell-1)!}{(n+\ell)!} \right]^{1/2}, \qquad \rho = \frac{2r}{a_0 n}\,.$$

Using that

$$x\, \frac{d}{dx}\, L^q_p(x) = (p+1)\;\, L^q_{p+1}(x) - (p+q+1-x)\;\, L^q_p(x)\,,$$

we have

$$r\, \frac{d}{dr}\, R_{n\ell}(r) = \left(\frac{r}{na_0} - n - 1 \right) R_{n\ell}(r) + \sqrt{(n-\ell)\,(n+\ell+1)}\; \frac{(n+1)^2}{n^2}\; R_{n+1,\ell}(r)\,.$$

All in all,

$$\begin{aligned}
\mathcal{R}_{fi} &= \frac{m}{\hbar}\,(E_f - E_i)\,\langle n_f\,\ell_f|\, f(r)\,|n_i\,\ell_i\rangle \\
&\quad + \frac{\hbar}{2}\, \Big\langle n_f\,\ell_f \Big|\, \Big[\, r f'' + 2\left(1 - n_i + \frac{r}{n_i a_0}\right) f' \,\Big] \Big| n_i\,\ell_i \Big\rangle \\
&\quad + \hbar\, \sqrt{(n_i - \ell_i)\,(n_i + \ell_i + 1)}\;\; \frac{(n_i+1)^2}{n_i^2}\;\, \langle n_f\,\ell_f|\, f'\, |n_i + 1, \ell_i\rangle
\end{aligned}$$

For $f(r) = r^s$, with s an integer, all the integrals in this expression are of the form (see Appendix A in [Galindo & Pascual])

$$\begin{aligned}
I_\alpha(pq; p'q') &:= \int_0^\infty dx\; e^{-x}\, x^\alpha\, L^q_p(x)\, L^{q'}_{p'}(x) \\
&= \alpha! \sum_{k=0}^{\min(p,p')} (-)^{p+p'+k} \binom{\alpha - q}{p-k} \binom{\alpha - q'}{p'-k} \binom{-\alpha - 1}{k}\,,
\end{aligned}$$

where the binomial coefficients are given by

$$\binom{q}{p} = \frac{q!}{p!\,(q-p)!} \quad \text{for} \quad q \geq p \geq 0$$

and

$$\binom{-q}{p} = (-)^p \binom{q+p-1}{p}\,, \quad \binom{q}{p} = 0 \quad \text{for} \quad p > q > 0\,.$$

PROBLEMA. El hamiltoniano de un sistema formado por dos partículas de masas m_1 y m_2 tiene la forma

$$H = \frac{\mathbf{P}_1^2}{2m_1} + \frac{\mathbf{P}_2^2}{2m_2} + V(|\mathbf{x}_1 - \mathbf{x}_2|)\,.$$

Los autoestados y autofunciones de H son conocidos. Durante un tiempo τ la partícula 2 experimenta una colisión que le comunica una velocidad $\mathbf{v}$. Supóngase que $\omega\tau << 1$ y que $|\mathbf{v}|\tau << a_0$, donde a_0 es el "tamaño clásico" del sistema. Si inicialmente el sistema se encuentra en su estado fundamental, cacular la probabilidad de que como consecuencia de la colisión el sistema salte al primer estado excitado.

Particularizar para el caso de un sistema unidimensional con una interacción vibratoria entre las partículas de frecuencia angular ω_0.

SOLUCIÓN (expresiones finales en rojo).

Before the 'kick', the system is a standard two-body problem. The positions and momenta of the center of mass (COM) and the 'reduced' (RED) particle are

$$\mathbf{R} = \frac{m_1\,\mathbf{x}_1 + m_2\,\mathbf{x}_2}{m_1 + m_2}\,, \qquad \mathbf{P} = \mathbf{p}_1 + \mathbf{p}_2\,,$$

$$\mathbf{r} = \mathbf{x}_1 - \mathbf{x}_2\,, \qquad \mathbf{p} = \frac{m_2\,\mathbf{p}_1 - m_1\,\mathbf{p}_2}{m_1 + m_2}\,,$$

with the total mass M and the reduced mass μ being given by

$$M = m_1 + m_2\,, \qquad \mu = \frac{m_1\,m_2}{m_1 + m_2}\,.$$

The hamiltonian H of the system can be writen as (the hats ˆ here denote operators)

$$H = \frac{\hat{\mathbf{P}}^2}{2M} + \frac{\hat{\mathbf{p}}^2}{2\mu} + V(|\mathbf{r}|)\,.$$

It can be splitted

$$H = H_{\text{COM}} + H_{\text{red}}\,,$$

in a center of mass part H_{COM} and a reduced part H_{RED},

$$H_{\text{COM}} = -\frac{\hbar^2}{2M}\,\Delta_{\mathbf{R}} \qquad H_{\text{RED}} = -\frac{\hbar^2}{2\mu}\,\Delta_{\mathbf{r}} + V(\mathbf{r})\,.$$

The total wave function is

$$\Psi(\mathbf{R},\mathbf{r},t) = e^{-i\,(E_{\text{COM}}t - \mathbf{P}\cdot\mathbf{R})/\hbar}\,\psi(\mathbf{r},t)\,,$$

with

$$E_{\text{COM}} = \frac{\mathbf{P}^2}{2M}$$

the COM energy and and $\psi(\mathbf{r},t)$ the solution to the reduced Schrödinger equation

$$i\hbar\,\frac{\partial}{\partial t}\,\psi(\mathbf{r},t) = H_{\text{RED}}\,\psi(\mathbf{r},t)\,.$$

The reduced stationary states are

$$\psi(\mathbf{r},t) = e^{-iE_{\text{RED}t/\hbar}t/\hbar}\,\phi(\mathbf{r})\,, \qquad H_{\text{RED}}\,\psi(\mathbf{r}) = E_{\text{RED}}\,\phi(\mathbf{r})\,.$$

After the 'kick', particle 2 has position $\mathbf{x}_2' = \mathbf{x}_2 + \mathbf{v}t$ and momentum $\mathbf{p}_2' = \mathbf{p}_2 + m_2\mathbf{v}$. The total hamiltonian becomes

$$\begin{aligned} H' &= \frac{\hat{\mathbf{P}}_1^2}{2m_1} + \frac{\hat{\mathbf{P}}_2^2}{2m_2} + \frac{1}{2}\,m_2\mathbf{v}^2 + \mathbf{P}_2\!\cdot\!\mathbf{v} + V(|\mathbf{x}_1 - \mathbf{x}_2 - \mathbf{v}t|) \\ &= \frac{\hat{\mathbf{P}}^2}{2M} + \frac{1}{2}\,m_2\mathbf{v}^2 + \frac{m_2}{M}\,\hat{\mathbf{P}}\!\cdot\!\mathbf{v} - \hat{\mathbf{p}}\!\cdot\!\mathbf{v} + \frac{\hat{\mathbf{p}}^2}{2\mu} + V(|\mathbf{r} - \mathbf{v}t|)\,. \end{aligned}$$

Its splitting

$$H' = H'_{\text{COM}} + H'_{\text{red}}$$

in COM and RED parts is now given by

$$\begin{aligned} H'_{\text{COM}} &= \frac{\hat{\mathbf{P}}^2}{2M} + \frac{1}{2}\,m_2\mathbf{v}^2 + \frac{m_2}{M}\,\hat{\mathbf{P}}\!\cdot\!\mathbf{v} \\ H'_{\text{RED}} &= -\hat{\mathbf{p}}\!\cdot\!\mathbf{v} + \frac{\hat{\mathbf{p}}^2}{2\mu} + V(|\mathbf{r} - \mathbf{v}t|)\,. \end{aligned}$$

The total wave function now reads

$$\Psi'(\mathbf{R},\mathbf{r},t) = e^{-i\,(E'_{\text{COM}}t - \mathbf{P}\cdot\mathbf{R})/\hbar}\,\psi'(\mathbf{r},t) \tag{4}$$

where the COM energy E'_{COM} is

$$E'_{\text{COM}} = \frac{\mathbf{P}^2}{2M} + \frac{1}{2}\,m_2\mathbf{v}^2 + \frac{m_2}{M}\,\mathbf{P}\!\cdot\!\mathbf{v}$$

and the reduced Schrödinger equation takes the form

$$i\hbar\,\frac{\partial}{\partial t}\,\psi'(\mathbf{r},t) = H'_{\text{RED}}\,\psi'(\mathbf{r},t)\,.$$

To remove the term $\hat{\mathbf{p}}\!\cdot\!\mathbf{v}$ from H'_{RED} , we make

$$\psi'(\mathbf{r},t) = e^{-i\mu\mathbf{v}\cdot\mathbf{r}/\hbar}\,\psi''(\mathbf{r},t)\,. \tag{5}$$

This gives

$$i\hbar\,\frac{\partial}{\partial t}\,\psi''(\mathbf{r},t) = \Big[-\frac{\hbar^2}{2\mu}\,\Delta_{\mathbf{r}} + V(|\mathbf{r} - \mathbf{v}t|)\Big]\,\psi''(\mathbf{r},t)\,. \tag{6}$$

We remark that Ψ' in eqs. (4)-(5) with ψ'' the solution to the Schrödinger equation (6) is the exact wave function after the kick. Note that there is no reason for the dependence of $\psi''(\mathbf{r},t)$ on t to be through $\mathbf{r}-\mathbf{v}t$. The approximations come next.

The sudden approximation establishes that the probability that the system jumps from a state i before the kick to a state f after the kick is given by

$$P = \left| \langle\, \Psi'_f(\mathbf{R},\mathbf{r},\tau) \,|\, \Psi_i(\mathbf{R},\mathbf{r},\tau) \,\rangle \right|^2 = \left| \langle\, e^{-i\mu\mathbf{v}\cdot\mathbf{r}/\hbar}\, \psi''_f(\mathbf{r},\tau) \,|\, \psi_i(\mathbf{r}) \,\rangle \right|^2 .$$

The states ψ''_f, that is, the solutions to the reduced time-dependent Schrödinger equation (6) after the kick do not follow from this approximation. We must find them by other means.

The region where the potential $V(\mathbf{r})$ is dominant is[1] $|\mathbf{r}| \sim a_0$. This and the assumption $|\mathbf{v}|\tau \ll a_0$ implies the approximation

$$\psi''_f(\mathbf{r},t) \approx e^{-iE_{\mathrm{RED}}t/\hbar}\, \psi_f(\mathbf{r}) \quad \text{for} \quad t \le \tau \ll \frac{a_0}{|\mathbf{v}|} ,$$

with $\{\psi_f(\mathbf{r}), E_{f,\mathrm{RED}}\}$ solutions for the unperturbed time-independent reduced hamiltonian H_{RED}. The pobability for the transition $\Psi_i(\mathbf{R},\mathbf{r},0) \to \Psi'_f(\mathbf{R},\mathbf{r},\tau)$ is then

$$P = \left| \langle\, e^{-i\mu\mathbf{v}\cdot\mathbf{r}/\hbar}\, \psi_f(\mathbf{r}) \,|\, \psi_i(\mathbf{r}) \,\rangle \right|^2 .$$

If the particles move in one dimension and interact through a harmonic oscillator potential, the reduced hamiltonian takes the form

$$H_{\mathrm{RED}} = -\frac{\hbar^2}{2\mu}\,\frac{d^2}{dx^2} + \frac{1}{2}\,\mu\omega^2 x^2 .$$

The wave functions ψ_i are

$$\psi_n(x) = \sqrt{\frac{\alpha}{\sqrt{\pi}\,2^n\,n!}}\; H_n(\alpha x)\; e^{-\alpha^2 x^2/2} , \qquad n = 0,1,\ldots , \qquad \alpha = \sqrt{\frac{\mu\omega}{\hbar}} ,$$

where $H_n(z)$ are the Hermite polynomials. If the oscillator is initially in its ground state, the probability for it to be in its first excited state after the kick is

$$P(v) = \left| \langle\, e^{-i\mu v x/\hbar}\, \psi_1(x) \,|\, \psi_0(x) \,\rangle \right|^2 = \frac{\mu v^2}{2\hbar\omega}\; e^{-\mu v^2/2\hbar\omega} .$$

The approximation is valid if $P \ll 1$. Since the exponential is bounded from above by 1, this requires $\frac{1}{2}\mu v^2 \ll \hbar\omega$, that is, the kinetic energy gained by particle 2 is much smaller than the energy of the ground state. In the regime $\frac{1}{2}\mu v^2 \gg \hbar\omega$ the probability also becomes very small.

Equating to zero the first derivative of $P(v)$ with respect to v, we have

$$P'(v_0) = 0 \quad \Rightarrow \quad \frac{1}{2}\,\mu v_0^2 = \hbar\omega .$$

[1] Recall, for example, that the probability density for the ground state of the hydrogen atom has its maximum at $|\mathbf{r}| = a_{\mathrm{Bohr}}$.

This corresponds to a maximum, since

$$P''(v_0) < 0\,.$$

The probability is then bounded from above by

$$P(v) \leq P(v_0) = e^{-1} \approx 0.368\,.$$

PROBLEMA. Un átomo de hidrógeno experimenta una transición $3p \to 2p$ emitiendo un fotón. Indicar de que tipo de transición se trata.

SOLUCIÓN (expresiones finales en rojo).

Let ℓ be the angular momentum of the operator $\mathcal{O}$ that mediates the transition

$$n_i = 3,\ \ell_i = 1,\ m_i \quad \to \quad n_f = 2,\ \ell_f = 1,\ m_f\,.$$

Composition of angular momenta,

$$\ell_i \otimes \ell \;=\; \ell_i + \ell, \ldots, |\ell_i - \ell| \;\ni\; \ell_f\,,$$

implies that

$$\begin{aligned} &1 \otimes 1 = 2,\ 1,\ 0 \\ &1 \otimes 2 = 3,\ 2,\ 1 \\ &1 \otimes \ell = \ell+1, \ldots, 2 \quad \text{for} \quad \ell \geq 3\,. \end{aligned}$$

The only allowed values for ℓ are then $\ell = 1, 2$. Since the initial and final states have the same parity, $\Pi_i = \Pi_f = -1$, the operator $\mathcal{O}$ must have $\Pi_{\mathcal{O}} = +1$. The case $\ell = 1$ corresponds to dipole magnetic transitions, and $\ell = 2$ to quadrupole electric transitions. The dipole magnetic transition amplitude is proportional to

$$(\mathbf{k} \wedge \boldsymbol{\epsilon})\ \langle n_f\, \ell_f\, m_f | \mathbf{L} | n_i\, \ell_i\, m_i \rangle = (\mathbf{k} \wedge \boldsymbol{\epsilon})\ \langle n_f\, \ell_f | n_i\, \ell_i \rangle\ \langle \ell_f\, m_f | \mathbf{L} | \ell_i\, m_i \rangle\,.$$

In the case at hand, $\ell_i = \ell_f$. Recalling that $\langle n_f\, \ell_i | n_i\, \ell_i \rangle = \delta_{n_i\, n_f}$, we conclude that the transition cannot be of this type. The amplitude for a quadrupole electric transition is proportional to

$$\sum_{i,j=1}^{3} k^i \epsilon^j\ \langle n_f\, \ell_f\, m_f | x^i\, x^j | n_i\, \ell_i\, m_i \rangle = \langle n_f\, \ell_f | r^2 | n_i\, \ell_i \rangle\ \sum_{i,j=1}^{3} k^i \epsilon^j\ \langle \ell_f\, m_f | \frac{x^i\, x^j}{r^2} | \ell_i\, m_i \rangle\,.$$

The angular integrals are different from zero. As for tha radial part we have

$$\langle 21 | r^2 | 31 \rangle = -\frac{2^{13}\, 3^5}{5^7}\ a_{\mathrm{B}}^2\ \neq 0\,.$$

Hence,

$$\ell = 2: \quad \text{Quadrupole electric transition.}$$

Comment. Higher multipole transitions are forbidden. Quadrupole magnetic transitions (M2) change parity, and octupole electric (E3) and magnetic (M3) do not allow $\ell_i = 1 \to \ell_f = 1$.

PROBLEMA. Sobre un oscilador armónico unidimensional de frecuencia angular ω, que en $t_i \to -\infty$ se encuentra en el estado fundamental, actua un campo externo cuya contribución al hamiltoniano es

$$V(x,t) = V_0 \left[\theta(x+vt) - \theta(x-vt) \right] .$$

Calcular la probabilidad de que salte al primer estado excitado ($t_f \to \infty$).

SOLUCIÓN (expresiones finales en rojo).

The transition probability in Born's approximation is

$$P^{(\mathrm{B})}_{i\to f} = \left| A^{(\mathrm{B})}_{i\to f} \right|^2 ,$$

where $A^{(\mathrm{B})}_{i\to f}$ is given by

$$A^{(\mathrm{B})}_{i\to f} = \frac{1}{\hbar} \int_{-\infty}^{\infty} dt \; e^{\mathrm{i}\,\omega_{fi}\, t}\, V_{fi} \,.$$

We first compute V_{fi}. At a given t, as a funtion of x, the perturbation $V(x,t)$ is rectangular pulse that extends from $-vt$ to vt. Hence

$$V_{fi} = V_0 \int_{-vt}^{vt} dx \; \psi_f^*(x) \; \psi_i(x)$$

The eigenfunctions and eigenvalues of the one-dimensional harmonic oscillator are

$$\psi_n(x) = \sqrt{\frac{\alpha}{\sqrt{\pi}\, 2^n \, n!}} \; H_n(\alpha x) \; e^{-\alpha^2 x^2/2} , \quad E_n = \hbar\omega \left(n + \frac{1}{2} \right) , \quad \alpha = \sqrt{\frac{\mu\omega}{\hbar}} , \quad n = 0, 1, \ldots$$

They have definite parity

$$\psi_n(-x) = (-)^n \, \psi_n(x) \,.$$

If $|i\rangle = |0\rangle$ and $|f\rangle = |1\rangle$, the matrix element $V_{fi} = V_{10}$ is the integral over a symmetric interval of an odd funtion, hence it vanishes,

$$V_{10} = 0 \,.$$

It follows that

$$P^{(\mathrm{B})}_{0\to 1} = 0 \,.$$

We move on to higher orders in perturbation theory. To nth order the amplitude $A^{(n)}_{i\to f}$ involves a chain of matrix elements

$$\sum_{k_1,\ldots,k_{n-1}} \langle f|V|k_{n-1}\rangle \;\; \langle k_{n-1}|V|k_{n-2}\rangle \;\; \cdots \;\; \langle k_1|V|i\rangle \,. \tag{7}$$

Since the perturbation V is even in x, the parity of $|i\rangle$ must be the same as that of $|k_1\rangle$, and this the same as that of $|k_2\rangle$, and so on. The final state $|f\rangle$ must then have the same parity as $|i\rangle$; otherwise the product (7) vanishes. We conclude that the transition amplitude for $|0\rangle \to |1\rangle$ is zero to all orders in perturbation theory,

$$P^{(n)}_{0\to 1} = 0 \,.$$

Comment 1. Assume $|i\rangle = |0\rangle$ and $|f\rangle = |2\rangle$. In this case,

$$V_{20} = \frac{V_0\,\alpha}{\sqrt{2\pi}} \int_{-vt}^{vt} dx\; \big(2\,\alpha^2 x^2 - 1\big) e^{-\alpha^2 x^2}\,.$$

Integrating by parts the first term in the integrand, we obtain

$$V_{20} = \sqrt{\frac{2}{\pi}}\; V_0 \alpha v t\; e^{-\alpha^2 v^2 t^2}\,.$$

It then follows that

$$A^{(\mathrm{B})}_{0\to 2} = \sqrt{\frac{2}{\pi}}\;\frac{V_0 \alpha v}{\hbar} \int_{-\infty}^{\infty} dt\; t\; e^{-\alpha^2 v^2 t^2}\; e^{2\mathrm{i}\omega t} = \frac{\mathrm{i}\,\sqrt{2}\;V_0\,\omega}{\hbar\,\alpha^2 v^2}\; e^{-\omega^2/\alpha^2 v^2}\,,$$

and from this

$$P^{(\mathrm{B})}_{0\to 2} = 2\left(\frac{V_0}{\mu v^2}\right)^2\; e^{-2\hbar\omega/\mu v^2}\,.$$

Born's approximation is valid if $P^{(\mathrm{B})}_{0\to 2} \ll 1$. This occurs for:

(i) $\hbar\omega \gg \mu v^2$. The exponential decreases very quickly and $P^{(\mathrm{B})}_{0\to 2}$ becomes very small. The quantity $\mu v^2/2$ can be thought of as a kinetic energy communicated by the pulse to the oscillating particle. It must be much smaller than the ground state energy $\hbar\omega/2$. This regime is independent of V_0.

(ii) $V_0 \ll \mu v^2$. That is, the height of the pulse is much smaller than the kinetic energy it communicates to the oscillator. Under this assumption, it is trivial that $P^{(\mathrm{B})}_{0\to 2} \ll 1$. This regime is independent of the relation between μv^2 and $\hbar\omega$.

Comment 2. An alternative approach is to integrate in $A^{(\mathrm{B})}_{i\to f}$ first over t and then over x. The easiest way to perform the integral over t is to use that the Fourier transform of the Heaviside function $\theta(s)$ is given by

$$\int_{-\infty}^{\infty} ds\; e^{\mathrm{i}\omega s}\;\theta(s) = \mathrm{i}\,\mathrm{PP}\,\frac{1}{\omega} + \pi\;\delta(\omega)\,.$$

This implies, after making the change $x \pm vt = s$, that

$$\int_{-\infty}^{\infty} dt\; e^{\mathrm{i}\,\omega_{fi}\,t}\;\theta(x\pm vt) = e^{\mp\mathrm{i}\,\omega_{fi}\,x/v}\left[\pm\,\mathrm{i}\,\mathrm{PP}\,\frac{1}{\omega_{fi}} + \pi\,\delta(\omega_{fi})\right].$$

Since by assumption ω_{fi} is different from zero, the Dirac delta does not contribute and the principal part can be removed. Hence

$$\int_{-\infty}^{\infty} dt\; e^{\mathrm{i}\omega_{fi}\,t}\big[\,\theta(x+vt) - \theta(x-vt)\,\big] = \frac{\mathrm{i}}{\omega_{fi}}\;\big(e^{-\mathrm{i}\,\omega_{fi} x/v} + e^{\,\mathrm{i}\,\omega_{fi} x/v}\big)\,.$$

With this, the amplitude in Born's approximation can be written as

$$A^{(\mathrm{B})}_{i\to f} = \frac{\mathrm{i}V_0}{\hbar\omega_{fi}} \int_{-\infty}^{\infty} dx \, \left(e^{-\mathrm{i}\,\omega_{fi} x/v} + e^{\,\mathrm{i}\,\omega_{fi} x/v} \right) \psi^*_f(x)\, \psi_i(x) \,. \tag{8}$$

Using for the Fourier transform of the function $f(x)$ at k the notation

$$\mathcal{F}\big[f(x)\big]\,(k) = \int_{-\infty}^{\infty} dx \; e^{ikx} \; f(x)\,,$$

the amplitude in (8) takes the form

$$A^{(\mathrm{B})}_{i\to f} = \frac{\mathrm{i}V_0}{\hbar\omega_{fi}} \; \mathcal{F}\big[\psi^*_f(x)\; \psi_i(x)\big]\big(\tfrac{\omega_{fi}}{v}\big) + (v \leftrightarrow -v)\,.$$

Note that if $\psi^*_f(x)\,\psi_i(x)$ is odd, the integral (8) vanishes, as we already know. For $\psi^*_f(x)\,\psi_i(x)$ even, both terms in (8) give the same contribution.

Comment 3. Consider now

$$V(x,t) = V_0 \left[\, 2\,\theta(x) - \theta(x+vt) - \theta(x-vt)\,\right].$$

It is very easy to show that in this case transitions occur between states with opposite parity.