PHY 742 Quantum Mechanics II
1-1:50 AM MWF Olin 103

Plan for Lecture 11

Time dependent perturbation theory
Ref: Chapter 15

1. **Introduction**
2. **Sudden approximation**
3. **Time harmonic perturbations**

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Topics for Quantum Mechanics II

Single particle analysis
- Single particle interacting with electromagnetic fields – EC Chap. 9
- Scattering of a particle from a spherical potential – EC Chap. 14
- More time independent perturbation methods – EC Chap. 12, 13
- Single electron states of a multi-well potential ➔ molecules and solids – EC Chap. 2,6
- Time dependent perturbation methods – EC Chap. 15
- Path integral formalism (Feynman) – EC Chap. 11.C
- Relativistic effects and the Dirac Equation – EC Chap. 16

Multiple particle analysis
- Quantization of the electromagnetic fields – EC Chap. 17
- Photons and atoms – EC Chap. 18
- Multi particle systems; Bose and Fermi particles – EC Chap. 10
- Multi electron atoms and materials
  - Hartree-Fock approximation
  - Density functional approximation

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Course schedule for Spring 2020

(Preliminary schedule -- subject to frequent adjustment.)

	Lecture date	Reading	Topic	HW	Due date
1	Mon: 01/13/2020	Chap. 9	Quantum mechanics of electromagnetic forces	#1	01/22/2020
2	Wed: 01/15/2020	Chap. 9	Quantum mechanics of particle in electrostatic field	#2	01/24/2020
3	Fri: 01/17/2020	Chap. 9	Quantum mechanics of particle in magnetostatic field	#3	01/27/2020
	Mon: 01/20/2020	No class	Martin Luther King Holiday		
4	Wed: 01/22/2020	Chap. 14	Scattering theory	#4	01/29/2020
5	Fri: 01/24/2020	Chap. 14	Scattering theory	#5	01/31/2020
6	Mon: 01/27/2020	Chap. 14	Scattering theory	#6	02/03/2020
7	Wed: 01/29/2020	Chap. 12	Variational methods	#7	02/05/2020
8	Fri: 01/31/2020	Chap. 12	Variational and other approximation methods	#8	02/07/2020
9	Mon: 02/03/2020	Chap. 2,6	Single particle states of molecules and solids	#9	02/10/2020
10	Wed: 02/05/2020	Chap. 2,6	H_2^+ molecular ion; Born Oppenheimer approximation	#10	02/12/2020
11	Fri: 02/07/2020	Chap. 15	Time-dependent perturbations	#11	02/14/2020
12	Mon: 02/10/2020				
13	Wed: 02/12/2020				
14	Fri: 02/14/2020				
15	Mon: 02/17/2020				
16	Wed: 02/19/2020				
17	Fri: 02/21/2020				

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Time dependence in quantum mechanics

Time dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t}|\psi\rangle = H|\psi\rangle$$

For the case that the Hamiltonian itself does not depend on time, we assume $|\psi(\mathbf{r},t)\rangle = \chi(\mathbf{r})e^{-iEt/\hbar}$

$$i\hbar \frac{\partial}{\partial t}|\psi\rangle = H|\psi\rangle \quad \Rightarrow \quad E\chi(\mathbf{r}) = H(\mathbf{r})\chi(\mathbf{r})$$

More generally, there are multiple solutions to the eigenvalue problem: $H(\mathbf{r})\chi_n(\mathbf{r}) = E_n\chi_n(\mathbf{r})$

$$\Rightarrow \quad |\psi(\mathbf{r},t)\rangle = \sum_n C_n\chi_n(\mathbf{r})e^{-iE_nt/\hbar}$$

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Sudden approximation

This method is useful when there is an abrupt change in the Hamiltonian of the system

Suppose that for $t < 0$, $H = H^A$

for $t > 0$, $H = H^B$

This can happen when we have a nuclear process occur which is "sudden" for the electronic states. It is also a reasonable approximation for some X-ray absorption processes in which an electron is suddenly removed from the core of an atom.

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Sudden approximation -- continued

The most convenient method to analyze this system is to find the complete sets of eigenvalues of the two Hamiltonians:

$$H^A|\psi_n^A\rangle = E_n^A|\psi_n^A\rangle$$

$$H^B|\psi_\nu^B\rangle = E_\nu^B|\psi_\nu^B\rangle$$

Suppose that at $t = 0$, $|\Psi(t=0)\rangle = |\psi_0^A\rangle$

It is reasonable to assume that for $t > 0$:

$$|\Psi(t>0)\rangle = \sum_\nu C_\nu|\psi_\nu^B\rangle e^{-iE_\nu^Bt/\hbar}$$

where $C_\nu = \langle\psi_\nu^B|\psi_0^A\rangle$

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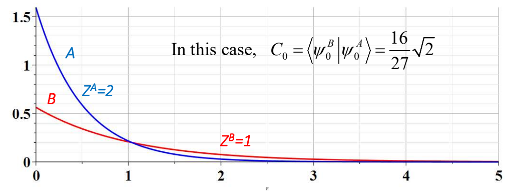
Example of a H-like ion initially with $Z^A=2$, transforming to one with $Z^B=1$.

Similar to HW #11



➔**Probability of H-like ion remaining in ground state:** $\left| \langle \psi_0^B | \psi_0^A \rangle \right|^2 \approx 70\%$

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Another example -- Harmonic oscillator with time varying frequency

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2(t)x^2$$

where $\omega^2(t) = \begin{cases} \omega_A^2 & \text{for } t < 0 \\ \omega_B^2 & \text{for } t > 0 \end{cases}$

Suppose that at $t = 0$, $|\Psi(t=0)\rangle = |\psi_0^A\rangle = \left(\frac{m\omega_A}{\pi\hbar}\right)^{1/4} e^{-m\omega_A x^2/(2\hbar)}$

Probability that system remains in ground state for $t > 0$:

with $|\psi_0^B\rangle = \left(\frac{m\omega_B}{\pi\hbar}\right)^{1/4} e^{-m\omega_B x^2/(2\hbar)}$

$$P = \left| \langle \psi_0^B | \psi_0^A \rangle \right|^2 = \frac{(4\omega_A\omega_B)^{1/4}}{(\omega_A + \omega_B)^{1/2}}$$

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Range of validity of sudden approximation

Sudden $\Rightarrow$ finite switching time Δt

Analysis neglects terms of magnitude $\frac{\Delta t |H_B - H_A|}{\hbar}$

For harmonic oscillator example, approximation assumes $\Delta t |\omega_B - \omega_A| \ll 1$

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Treatment of time-dependent perturbations

$$i\hbar\frac{\partial}{\partial t}\left|\psi\right\rangle = H(t)\left|\psi\right\rangle$$
$$H(t) = H^0 + \epsilon H^1(t)$$

We approach the problem using the complete basis set of H^0 :

$$H^0\left|n^0\right\rangle = E_n^0\left|n^0\right\rangle$$

It is reasonable to assume that

$$\left|\psi(t)\right\rangle = \sum_n c_n(t)\left|n^0\right\rangle \equiv \sum_n k_n(t)e^{-iE_n^0 t/\hbar}\left|n^0\right\rangle$$

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Treatment of time-dependent perturbations -- continued

$$\left|\psi(t)\right\rangle = \sum_n k_n(t)e^{-iE_n^0 t/\hbar}\left|n^0\right\rangle$$
$$i\hbar\frac{\partial}{\partial t}\left|\psi\right\rangle = \left(H^0 + \epsilon H^1(t)\right)\left|\psi\right\rangle$$
$$\sum_n\left(i\hbar\frac{dk_n(t)}{dt} - \epsilon H^1(t)k_n(t)\right)e^{-iE_n^0 t/\hbar}\left|n^0\right\rangle = 0$$

Projecting this equation with a particular zero-order state $\left\langle f^0\right|$:

$$i\hbar\frac{dk_f(t)}{dt} = \epsilon\sum_n\left\langle f^0\right|H^1(t)\left|n^0\right\rangle k_n(t)e^{i\left(E_f^0 - E_n^0\right)t/\hbar}$$

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Treatment of time-dependent perturbations -- continued

$$i\hbar\frac{dk_f(t)}{dt} = \epsilon\sum_n\left\langle f^0\right|H^1(t)\left|n^0\right\rangle k_n(t)e^{i\left(E_f^0 - E_n^0\right)t/\hbar}$$

Perturbation expansion for time-dependent coefficients:

$$k_n(t) = k_n^0 + \epsilon k_n^1(t) + \epsilon^2 k_n^2(t) + \ldots$$

Zero order equation: $\frac{dk_n^0}{dt} = 0$

s-order equation for $s > 0$:

$$\frac{dk_m^s}{dt} = \frac{1}{i\hbar}\sum_n\left\langle m^0\right|H^1(t)\left|n^0\right\rangle k_n^{s-1}(t)e^{i\left(E_m^0 - E_n^0\right)t/\hbar}$$

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Treatment of time-dependent perturbations -- continued

1^{st}-order equation, assuming that $k_n^0 = \delta_{nI}$

$$\frac{dk_m^1}{dt} = \frac{1}{i\hbar}\left\langle m^0 \left| H^1(t) \right| I^0 \right\rangle e^{i\left(E_m^0 - E_I^0\right)t/\hbar}$$

Example:

Suppose that $H^1(t) = \tilde{H}^1 h(t)$

$$\text{where} \qquad h(t) \equiv \begin{cases} 0 & \text{for } t<0 \text{ and } t>T \\ 2\sin\omega t & \text{for } 0<t<T \end{cases}$$

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Treatment of time-dependent perturbations -- continued

For this example

$$\frac{dk_m^1}{dt} = 0 \quad \text{for } t<0 \text{ or } t>T$$

$$\frac{dk_m^1}{dt} = \frac{2}{i\hbar}\frac{\left\langle m^0 \left| \tilde{H}^1 \right| I^0 \right\rangle}{2i}\left(e^{i(\omega+\omega_{mI})t} - e^{i(-\omega+\omega_{mI})t}\right)$$

$$\text{for } 0<t<T$$

$$\Rightarrow k_m^1(t) = \frac{2}{i\hbar}\frac{\left\langle m^0 \left| \tilde{H}^1 \right| I^0 \right\rangle}{2}\left(\frac{e^{i(\omega+\omega_{mI})T}-1}{\omega+\omega_{mI}} - \frac{e^{i(-\omega+\omega_{mI})T}-1}{-\omega+\omega_{mI}}\right)$$

where $\omega_{mI} \equiv \left(E_m^0 - E_I^0\right)/\hbar$ for $t>T$

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For $t>T$

$$k_m^1(t) = \frac{2}{i\hbar}\frac{\left\langle m^0 \left| \tilde{H}^1 \right| I^0 \right\rangle}{2}\left(\frac{e^{i(\omega+\omega_{mI})T}-1}{\omega+\omega_{mI}} - \frac{e^{i(-\omega+\omega_{mI})T}-1}{-\omega+\omega_{mI}}\right)$$

where $\omega_{mI} \equiv \left(E_m^0 - E_I^0\right)/\hbar$

$$\left|k_m^1(t)\right|^2 \approx \frac{4}{\hbar^2}\left|\left\langle m^0 \left| \tilde{H}^1 \right| I^0 \right\rangle\right|^2 \times$$

$$\left(\frac{\sin^2\left((\omega+\omega_{mI})T/2\right)}{\left(\omega+\omega_{mI}\right)^2} + \frac{\sin^2\left((-\omega+\omega_{mI})T/2\right)}{\left(-\omega+\omega_{mI}\right)^2}\right)$$

$$\approx \frac{4\pi T}{2\hbar^2}\left|\left\langle m^0 \left| \tilde{H}^1 \right| I^0 \right\rangle\right|^2 \left(\delta\left(\omega+\omega_{mI}\right) + \delta\left(-\omega+\omega_{mI}\right)\right)$$

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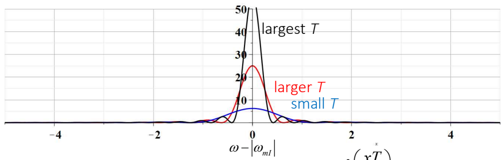
Treatment of time-dependent perturbations -- continued

Behavior of $k_m^1(T)$ in the neighborhood of $\omega = |\omega_{mI}|$



Note that $\int_{-\infty}^{\infty} \frac{\sin^2\left(\frac{xT}{2}\right)}{x^2} dx = \frac{\pi T}{2}$

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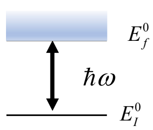
Estimating the rate of transitions $I \rightarrow f$

$$\mathcal{R}_{I\to f} = \frac{\left|k^1_{I\to f}(t)\right|^2}{T} \approx \frac{2\pi}{\hbar}\left|\langle f^0|\tilde{H}^1|I^0\rangle\right|^2 \left(\delta\left(\hbar\omega + E_f^0 - E_I^0\right) + \delta\left(-\hbar\omega + E_f^0 - E_I^0\right)\right)$$

Fermi "Golden" rule



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Example

H atom in presence of electric field

$\tilde{H}^1 = -eFz$ representing field as scalar potential

$\tilde{H}'^1 = \frac{ecFp_z}{i\omega mc}$ representing field as vector potential

Note that these two are equivalent in the ideal case:

$$\frac{p_z}{m} = \frac{1}{i\hbar}\left[z, \frac{\mathbf{p}^2}{2m}\right] = \frac{1}{i\hbar}\left[z, H^0\right]$$

$$\langle f^0|\frac{p_z}{m}|I^0\rangle = \frac{1}{i\hbar}\langle f^0|\left[z, H^0\right]|I^0\rangle = -\frac{E_f^0 - E_I^0}{i\hbar}\langle f^0|z|I^0\rangle$$

$$= i\omega_{fI}\langle f^0|z|I^0\rangle$$

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Example

H atom in presence of electric field

$$\tilde{H}^1 = -eFz \quad \text{representing field as scalar potential}$$
$$= -eFr\cos\theta$$

Some H^0 eigenstates for H-like ion:

$$\left|I^0 = 1s\right\rangle = \left(\frac{Z^3}{a_0^3\pi}\right)^{1/2} e^{-Zr/a_0} \qquad E_I^0 = -\frac{Z^2e^2}{2a_0}$$

$$\left|f^0 = 2p_0\right\rangle = \left(\frac{Z^3}{32a_0^3\pi}\right)^{1/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \cos\theta \qquad E_f^0 = -\frac{Z^2e^2}{2a_0}\frac{1}{4}$$

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$$\left\langle f^0\left|\tilde{H}^1\right|I^0\right\rangle = \left\langle f^0\left|-eFr\cos\theta\right|I^0\right\rangle$$

H^0 eigenstates for H-like ion: $\left|I^0 = 1s\right\rangle = \left(\frac{Z^3}{a_0^3\pi}\right)^{1/2} e^{-Zr/a_0}$

$$\left|f^0 = 2p_0\right\rangle = \left(\frac{Z^3}{32a_0^3\pi}\right)^{1/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \cos\theta$$

$$\left\langle f^0\left|\tilde{H}^1\right|I^0\right\rangle = -eF\frac{Z^3}{a_0^3\pi}\left(\frac{1}{32}\right)^{1/2} 2\pi\frac{2}{3}\int_0^\infty r^3 dr \frac{Zr}{a_0} e^{-3Zr/2a_0}$$
$$= -eF\frac{Z^3}{a_0^3\pi}\left(\frac{1}{32}\right)^{1/2} 2\pi\frac{2}{3}\left(\frac{a_0}{Z}\right)^4 \int_0^\infty x^4 dx\, e^{-\frac{3}{2}x}$$
$$= -\frac{eFa_0}{\sqrt{2}Z}\frac{256}{243}$$

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Summary of results for resonant transitions for H-like ion ***$1s \rightarrow 2p_0$***

$$\mathcal{R}_{I\to f} \approx \frac{2\pi}{\hbar}\left|\left\langle f^0\left|\tilde{H}^1\right|I^0\right\rangle\right|^2 \delta\left(-\hbar\omega + E_f^0 - E_I^0\right)$$

$$\left\langle f^0\left|\tilde{H}^1\right|I^0\right\rangle = -\frac{eFa_0}{\sqrt{2}Z}\frac{256}{243}$$

$$\hbar\omega = E_f^0 - E_I^0 = \frac{3}{4}\frac{Z^2e^2}{2a_0} = 10.204\, Z^2 \text{ eV}$$

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Digression: Notion of oscillator strength for transition between states $I \rightarrow n$:

$$f_{nI} = \frac{2m}{\hbar^2}\left(E_n^0 - E_I^0\right)\left|\left\langle n^0 \right| z \left| I^0 \right\rangle\right|^2$$

$$\left[z,\left[z,H^0\right]\right] = z^2 H^0 + H^0 z^2 - 2zH^0 z = \frac{i\hbar}{m}\left[z, p_z\right] = -\frac{\hbar^2}{m}$$

$$\left\langle I^0 \right|\left[z,\left[z,H^0\right]\right]\left| I^0 \right\rangle = 2E_I^0 \left\langle I^0 \right| z^2 \left| I^0 \right\rangle - 2\left\langle I^0 \right| zH^0 z \left| I^0 \right\rangle = -\frac{\hbar^2}{m}$$

Inserting resolution of the identity: $1 = \sum_n \left| n^0 \right\rangle \left\langle n^0 \right|$

$$\sum_n \left(2E_I^0 \left\langle I^0 \right| z \left| n^0 \right\rangle \left\langle n^0 \right| z \left| I^0 \right\rangle - 2\left\langle I^0 \right| z \left| n^0 \right\rangle E_n^0 \left\langle n^0 \right| z \left| I^0 \right\rangle \right) = -\frac{\hbar^2}{m}$$

$$\frac{2m}{\hbar^2}\sum_n \left(E_n^0 - E_I^0\right)\left\langle I^0 \right| z \left| n^0 \right\rangle \left\langle n^0 \right| z \left| I^0 \right\rangle = \sum_n f_{nI} = 1$$ **sum rule for oscillator strength**

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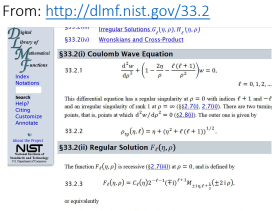
Absorption of radiation in the case of photo emission

$$\left| f^0 \right\rangle = R_{El}(r) Y_{lm}(\hat{\mathbf{r}})$$

$$\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{l(l+1)}{r^2} + \frac{Ze^2}{r} + E \right) R_{El}(r) = 0$$

From: http://dlmf.nist.gov/33.2


Digital Library of Mathematical Functions

§33.2(iii) Irregular Solutions $G_\ell(\eta,\rho), H_\ell^{\pm}(\eta,\rho)$

§33.2(iv) Wronskians and Cross-Product

§33.2(i) Coulomb Wave Equation

33.2.1 $$\frac{d^2 w}{d\rho^2} + \left(1 - \frac{2\eta}{\rho} - \frac{\ell(\ell+1)}{\rho^2}\right) w = 0, \quad \ell = 0, 1, 2, \ldots$$

This differential equation has a regular singularity at $\rho = 0$ with indices $\ell + 1$ and $-\ell$ and an irregular singularity of rank 1 at $\rho = \infty$ (§§2.7(i), 2.7(ii)). There are two turning points, that is, points at which $d^2 w / d\rho^2 = 0$ (§2.8(i)). The outer one is given by

33.2.2 $$\rho_{tp}(\eta,\ell) = \eta + (\eta^2 + \ell(\ell+1))^{1/2}.$$

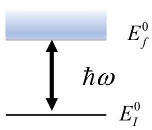
§33.2(ii) Regular Solution $F_\ell(\eta,\rho)$

The function $F_\ell(\eta,\rho)$ is recessive (§2.7(iii)) at $\rho = 0$, and is defined by

33.2.3 $$F_\ell(\eta,\rho) = C_\ell(\eta) 2^{-\ell-1} (\mp i)^{\ell+1} M_{\pm i\eta, \ell+\frac{1}{2}}(\pm 2 i \rho),$$

or equivalently

33.2.4 $$F_\ell(\eta,\rho) = C_\ell(\eta) \rho^{\ell+1} e^{\mp i\rho} M(\ell + 1 \mp i\eta, 2\ell + 2, \pm 2 i \rho),$$



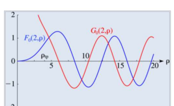


Figure 33.3.3: $F_\ell(\eta,\rho)$, $G_\ell(\eta,\rho)$ with $\ell = 0$, $\eta = 2$. The turning point is at $\rho_{tp}(2,0) = 4$.

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Absorption of radiation in the case of photo emission
approximating final state as a plane wave (Born approximation)

$$\left| f^0 \right\rangle \approx \mathcal{N} e^{i\mathbf{k}\cdot\mathbf{r}} \quad \text{where } k = \sqrt{(2mE/\hbar^2)}$$

For initial state: $\left| I^0 = 1s \right\rangle = \left(\frac{Z^3}{a_0^3 \pi} \right)^{1/2} e^{-Zr/a_0}$

$$\mathcal{R}_{I\to f} \approx \frac{2\pi}{\hbar} \left| \left\langle f^0 \right| \tilde{H}^1 \left| I^0 \right\rangle \right|^2 \delta\left(-\hbar\omega + E_f^0 - E_I^0\right)$$

$$\left\langle f^0 \right| \tilde{H}^1 \left| I^0 \right\rangle = \left\langle f^0 \right| -eFr\cos\theta \left| I^0 \right\rangle$$

Note: In a more accurate treatment, one should modify the static electric field in order to account for electrodynamics …

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For a H-like ion in a beam of photons with flux *S*, it is convenient to define a cross section:

$$\int d\omega \frac{d\sigma(\omega)}{d\Omega} = \int d\omega \frac{\mathcal{R}_{I\to f}(\omega)}{S(\omega)}$$

For a final state electron in

the $\hat{\mathbf{k}}$ direction and a photon directed toward $\hat{\mathbf{z}}$:

$$\frac{d\sigma(\omega)}{d\Omega} = \frac{32 e^2 k^3 \cos^2\theta}{mc\omega} \frac{Z^5}{a_0^5} \frac{1}{\left(\frac{Z^2}{a_0^2} + k^2 + \frac{\omega^2}{c^2} - 2k\frac{\omega}{c}\cos\theta\right)^4}$$

(Details: Merzbacher, Quantum Mechanics, third ed. (1998)

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