# MAU34404 - Quantum Mechanics II
# Brief Notes

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## 1 Rotations and Angular Momentum

### 1.1 Infinitesimal Rotations

Rotation about the $z$-axis in a positive clockwise direction by an angle $\phi$ is characterised by

$$R_z(\phi) = \begin{pmatrix} \cos\phi & -\sin\phi & 0 \\ \sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

For $\phi \simeq \varepsilon << 1$ (an infinitesimal rotation), this becomes

$$R_z(\varepsilon) = \mathbb{1} + \varepsilon \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} + \varepsilon^2 \begin{pmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

The equivalent infinitesimal rotations about the $x$ and $y$ axes are

$$R_x(\varepsilon) = \mathbb{1} + \varepsilon \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix} + \varepsilon^2 \begin{pmatrix} 0 & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & -\frac{1}{2} \end{pmatrix},$$

$$R_y(\varepsilon) = \mathbb{1} + \varepsilon \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{pmatrix} + \varepsilon^2 \begin{pmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -\frac{1}{2} \end{pmatrix}.$$

These yield the relation

$$R_x(\varepsilon)R_y(\varepsilon) - R_y(\varepsilon)R_x(\varepsilon) = R_z(\varepsilon^2) - \mathbb{1},$$

i.e. rotations to not commute.

### 1.2 Unitary Rotation Operator

We define the operator corresponding to a rotation transforming the state $|\psi\rangle$ into the state $|\psi'\rangle$ as

$$|\psi'\rangle = \mathcal{U}_R |\psi\rangle .$$

This operator is not generally a 3×3 orthogonal matrix like $R$, but rather depends on the dimensionality of the space. We expect that for a continuous transformation - like an infinitesimal rotation - the state $|\psi\rangle$ will be almost unchanged. So,

$$\mathcal{U}_\varepsilon = \mathbb{1} - iG\varepsilon$$

for an operator $G$. We can show that for $\mathcal{U}$ to be unitary ($\mathcal{U}\mathcal{U}^\dagger = \mathbb{1}$), $G$ must be Hermitian, i.e. $G = G^\dagger$, where † is the conjugate transpose. For clarity of notation, we let $G = \dfrac{\vec{J}\cdot\hat{n}}{\hbar}$ and $\varepsilon = d\phi$, where $\vec{J}$ is the angular momentum vector and $\hat{n}$ is the unit vector in the direction of the axis of rotation. e.g. for a rotation about the $z$-axis, $\hat{n} = \hat{z}$, so $\vec{J}\cdot\hat{n} = \vec{J}\cdot\hat{z} = J_z$.

### 1.3 The Fundamental Commutation Relation of Angular Momentum

We can make a finite rotation by an angle $\phi$ by making a series of $N$ rotations by angles $d\phi$ such that $d\phi = \dfrac{\phi}{N}$. Thus,

$$\mathcal{U}_{R(\phi)} = \mathcal{U}^N_{R(d\phi)} = \left[\mathbb{1} - \frac{i}{\hbar}\vec{J}\cdot\hat{n}d\phi\right]^N = \left[\mathbb{1} - \frac{i}{\hbar}\vec{J}\cdot\hat{n}\frac{\phi}{N}\right]^N .$$

Taking the limit $N \to \infty$, we get the definition

$$\mathcal{U}_{R(\phi)} = e^{-i\vec{J}\cdot\hat{n}\phi/\hbar} \iff \exp\left(-\frac{i}{\hbar}\vec{J}\cdot\hat{n}\phi\right).$$

Remember that we must still satisfy the commutation relation $[R_x(\varepsilon), R_y(\varepsilon)] = R_z(\varepsilon^2) - \mathbb{1}$. This leads to the fundamental commutation relation of angular momentum:

$$[J_i, J_j] = i\hbar\epsilon_{ijk}J_k.$$

### 1.4 Spin Angular Momentum and Fermions

In general, the total angular momentum $\vec{J}$ is composed of orbital angular momentum $\vec{L}$ and spin angular momentum $\vec{\mathcal{S}}$. The spin angular momentum $\vec{\mathcal{S}}$ of spin-$\frac{1}{2}$ particles (all fermions e.g. electrons, protons, neutrons, quarks, neutrinos, etc.) can be represented in terms of the Pauli matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},$$

which are Hermitian and unitary. These matrices (along with the identity) form a complete basis for the real $2 \times 2$ Hermitian matrices. The Pauli matrices correspond to measuring the spin of the particle along their respective axes. The eigenvalues of the Pauli matrices are $\pm 1$, corresponding to observing spin “up” or spin “down”.

The components of the spin angular momentum are

$$\mathcal{S}_i = \frac{\hbar}{2}\sigma_i, \quad i = x, y, z.$$

## 2 Symmetries and Representation Theory

### 2.1 Rotational Symmetries

Consider a Hamiltonian $\mathcal{H}$ parametrised by some parameters $\alpha$ (position, momentum, etc.) satisfying the Schrödinger equation

$$i\hbar\frac{\partial|\psi(t)\rangle}{\partial t} = \mathcal{H}(\alpha)\,|\psi(t)\rangle\,.$$

If under a rotation a new Hamiltonian is $\mathcal{H}(\alpha_R)$, then (assuming the system is invariant) we have

$$i\hbar\frac{\partial\mathcal{U}_R\,|\psi(t)\rangle}{\partial t} = \mathcal{H}(\alpha_R)\mathcal{U}_R\,|\psi(t)\rangle\,.$$

Assuming that $\mathcal{U}_R$ is time-independent, then

$$i\hbar\frac{\partial|\psi(t)\rangle}{\partial t} = \mathcal{U}_R^\dagger\mathcal{H}(\alpha)\mathcal{U}_R\,|\psi(t)\rangle \implies \mathcal{H}(\alpha_R) = \mathcal{U}_R\mathcal{H}(\alpha)\mathcal{U}_R^\dagger$$

Thus, a rotation invariant Hamiltonian ($\mathcal{H}(\alpha_R) = \mathcal{H}(\alpha)$) satisfies $[\mathcal{H},\mathcal{U}_R] = 0$. Further, using our definiton of $\mathcal{U}_R$, we know $[\mathcal{H}, \vec{J}] = 0$. The total angular momentum is a constant of motion.

## 2.2 Symmetry Transformations

A symmetry transformation corresponding to a unitary operator (as opposed to anti-unitary operators, which correspond to discontinuous transformations e.g. spatial inversion) acts on a state

$$|\psi\rangle \to |\psi_a\rangle$$

by a unitary operator $\mathcal{U}_a$ as $|\psi_a\rangle = \mathcal{U}_a |\psi\rangle$ such that $\mathcal{U}_{ab} = \mathcal{U}_a\mathcal{U}_b$. If we introduce a complete basis for our Hilbert space $\mathbb{H}$, we can represent this transformation as a matrix whose elements are

$$\mathcal{D}_{ij}(a) = \langle i| \mathcal{U}_a |j\rangle \,, \quad i,j = 1,2,...,\dim(\mathbb{H}) = n.$$

In this form, a rotation would be represented as

$$\mathcal{D}^{(j)}_{mm'}(R) = \langle jm'| \mathcal{U}_R |jm\rangle \,.$$

See Tutorial 1 for the rest of this example.

Composing symmetry transformations, we see that

$$\mathcal{D}_{ij}(ab) = \langle i| \mathcal{U}_{ab} |j\rangle = \langle i| \mathcal{U}_a\mathcal{U}_b |j\rangle$$

Inserting a complete set of states (the identity) $\mathbb{1} = \sum\limits_k |k\rangle \langle k|$, we get

$$\mathcal{D}_{ij}(ab) = \sum_k \langle i| \mathcal{U}_a |k\rangle \langle k| \mathcal{U}_b |j\rangle = \sum_k \mathcal{D}_{ik}(a)\mathcal{D}_{kj}(b)$$

Thus, we have the condition of a group homomorphism:

$$\mathcal{D}_{ij}(ab) = \mathcal{D}_{ij}(a)\mathcal{D}_{ij}(b).$$

The symmetry transformations preserve the algebraic structure of the group.

## 2.3 Equivalent and Irreducible Representations

If we choose a different basis for our space, e.g. $|\tilde{i}\rangle = S_{ji} |j\rangle$, then

$$\begin{aligned} \widetilde{\mathcal{D}}_{ij} &= \langle \tilde{i}| \mathcal{U}_a |\tilde{j}\rangle = S^{-1}_{ik}\mathcal{D}_{kl}S_{lj} \\ &\implies \widetilde{\mathcal{D}} = S^{-1}\mathcal{D}S. \end{aligned}$$

Any representations related by a change of basis (a "similarity transformation") are called "equivalent representations" which are isomorphic to one another. If, by means of a similarity transformation, we can write a representation matrix in a block diagonal form, e.g.

$$\mathcal{D}(a) = \left[\begin{array}{c|c|c} \mathcal{D}_1(a) & 0 & 0 \\ \hline 0 & \mathcal{D}_2(a) & 0 \\ \hline 0 & 0 & \mathcal{D}_3(a) \end{array}\right],$$

then $\mathcal{D}_1, \mathcal{D}_2, \mathcal{D}_3$, all form lower-dimensional representations. In this way, the original representation has been reduced into a number of smaller representations and is said to be "reducible".

If no basis can be found to simultaneously reduce all $\mathcal{D}(a)$ in a representation, then it is said to be "irreducible". Up to similarity transformations, the decomposition of a representation into irreducible representations ("irreps") is unique.

This is useful, because we can now shift our coordinate systems in such a way as to make a given system easier to solve. Think changing from Cartesian to spherical coordinates to solve a spherically symmetric problem. We can exploit symmetries by performing a transformation into a coordinate system that makes the problem easier to solve. We can classify all stationary states of a Hamiltonian by irreps to which the eigenvectors of the Hamiltonian belong.

## 2.4 Addition of Angular Momenta

Consider two distinct systems which both have angular momentum (e.g. the spin and orbit contributions of an electron, or a Hydrogen atom with an electron and proton). If these distinct systems are described by the vector spaces $\{|i_1\rangle_{i_1=1_1,\ldots,n_1}, \ |i_2\rangle_{i_2=1_2,\ldots,n_2}\}$ and are then combined, the total space is spanned by all vectors of the form $|i_1\rangle \otimes |i_2\rangle$, which is (at most) $n_1 n_2$-dimensional.

A transformation of the two systems by a common rotation is given by

$$\begin{aligned}\mathcal{D}^{j_1} \otimes \mathcal{D}^{j_2} &= \exp\left(-\frac{i}{\hbar}\hat{n}\cdot\vec{J}_1\phi\right) \otimes \exp\left(-\frac{i}{\hbar}\hat{n}\cdot\vec{J}_2\phi\right) \\ &= \exp\left(-\frac{i}{\hbar}\hat{n}\cdot(\vec{J}_1\otimes\mathbb{1} + \mathbb{1}\otimes\vec{J}_2)\phi\right) \\ &= \exp\left(-\frac{i}{\hbar}\hat{n}\cdot\vec{J}\phi\right)\end{aligned}$$

where we let the total angular momentum $\vec{J} = \vec{J}_1 \otimes \mathbb{1} + \mathbb{1} \otimes \vec{J}_2$. If system 1 has $J_1^2$ eigenvalues of $j_1(j_1+1)\hbar^2$ and system 2 has $J_2^2$ eigenvalues of $j_2(j_2+1)\hbar^2$, i.e. system 1 has a basis $|j_1 m_1\rangle$ and system 2 has a basis $|j_2 m_2\rangle$, then $\vec{J}$ is $(2j_1+1)(2j_2+1) \times (2j_1+1)(2j_2+1)$-dimensional.

A common basis for the combined system is

$$|j_1 j_2 m_1 m_2\rangle = |j_1 m_1\rangle \otimes |j_2 m_2\rangle$$

however, this basis does not necessarily diagonalise $\vec{J}$, as we would like. We need to find a basis for which the total angular momentum $\vec{J}$ is block-diagonal. This basis is

$$|j_1 j_2 j m\rangle = \sum_{m_1=-j_1}^{j_1} \sum_{m_2=-j_2}^{j_2} |j_1 j_2 m_1 m_2\rangle \langle j_1 j_2 m_1 m_2 | j_1 j_2 j m\rangle$$

where the quantities $\langle j_1 j_2 m_1 m_2 | j_1 j_2 j m\rangle$ are the Clebsch-Gordan coefficients. For clarity, these states are usually written as

$$|j_1 j_2 j m\rangle = |jm\rangle\,, \quad |j_1 j_2 m_1 m_2\rangle = |m_1 m_2\rangle\,.$$

Both $|jm\rangle$ and $|m_1 m_2\rangle$ are eigenstates of $J_z$, so they must either have the same eigenvalues or be orthogonal. Thus, we must have $\langle m_1 m_2 | J_z |jm\rangle = m\,|jm\rangle$ (acting to the right) and $\langle m_1 m_2 | J_z |jm\rangle = (m_1+m_2)\,|m_1 m_2\rangle$ (acting to the left). This gives the condition

$$m = m_1 + m_2 \quad \text{or} \quad \langle m_1 m_2 | jm\rangle = 0,$$

leading to the "triangular condition" on $j$ that

$$|j_1 - j_2| \le j \le j_1 + j_2.$$

$m = m_1 + m_2$ ranges in integer steps from $-j$ to $j$, so $j$ ranges in half-integer steps from $|j_1 - j_2|$ to $j_1 + j_2$. The total number of allowed states is $(2j_1+1)(2j_2+1)$.

# 3 Time-Independent Perturbation Theory

## 3.1 Non-Degenerate Perturbation Theory

We want to consider systems with a Hamiltonian

$$\mathcal{H} = \mathcal{H}^{(0)} + gV$$

where $\mathcal{H}^{(0)}$ is a Hamiltonian with known eigenvectors and eigenvalues $\mathcal{H}^{(0)} |\psi_n^{(0)}\rangle = E_n^{(0)} |\psi_n^{(0)}\rangle$ and $V$ is some potential regulated by a small parameter $g << 1$. We want to find $\mathcal{H}|\psi_n\rangle = E_n |\psi_n\rangle$ for the total system.

We assume that there is no degeneracy in the known energy levels, i.e. $E_n^{(0)} \neq E_m^{(0)}$, and that we can write the energies and eigenstates of the full system in terms of a power series in $g$, namely

$$E_n = E_n^{(0)} + gE_n^{(1)} + g^2 E_n^{(2)} + ...$$

$$|\psi_n\rangle = |\psi_n^{(0)}\rangle + g|\psi_n^{(1)}\rangle + g^2 |\psi_n^{(2)}\rangle + ...$$

At order $g$, we have

$$\mathcal{H}^{(0)} |\psi_n^{(1)}\rangle + V|\psi_n^{(0)}\rangle = E_n^{(1)} |\psi_n^{(0)}\rangle + E_n^{(0)} |\psi_n^{(1)}\rangle .$$

Acting with $\langle\psi_m^{(0)}|$, we get

$$E_m^{(1)}\delta_{nm} = V_{nm} + (E_m^{(0)} - E_n^{(0)}) \langle\psi_m^{(0)}|\psi_n^{(1)}\rangle ,$$

where $V_{nm} := \langle\psi_m^{(0)}| V |\psi_n^{(0)}\rangle$. When $n = m$, we get the first correction to the energy

$$E_n^{(1)} = V_{nn} = \langle\psi_n^{(0)}| V |\psi_n^{(0)}\rangle .$$

We now have

$$(\mathcal{H}^{(0)} - E_n^{(0)}) |\psi_n^{(1)}\rangle = (E_n^{(1)} - V) |\psi_n^{(0)}\rangle$$

which is an eigenvalue problem $A\vec{v} = \lambda\vec{v}$. Expanding $|\psi_n^{(1)}\rangle = \sum\limits_{n\neq m} c_n^m |\psi_m^{(0)}\rangle$ in the basis $|\psi_n^{(0)}\rangle$, we get

$$\sum_{n\neq m} (E_m^{(0)} - E_n^{(0)}) c_n^m |\psi_m^{(0)}\rangle = (E_m^{(1)} - V) |\psi_n^{(0)}\rangle .$$

Acting with $\left\langle\psi_l^{(0)}\right|$ picks out the $l = m$ term and yields

$$(E_l^{(0)} - E_n^{(0)}) c_l^n = -\langle\psi_l^{(0)}| V |\psi_n^{(0)}\rangle \implies c_n^l = -\frac{V_{ln}}{E_l^{(0)} - E_n^{(0)}} .$$

Thus, the first correction to the eigenstates is

$$|\psi_n^{(1)}\rangle = \sum_{m\neq n} \frac{V_{nm}}{E_n^{(0)} - E_m^{(0)}} |\psi_m^{(0)}\rangle .$$

## 3.2 Degenerate Perturbation Theory

Degenerate perturbation theory is required if $E_n^{(0)} \simeq E_m^{(0)}$ for $n \neq m$, i.e. for energies that are close together or perfectly degenerate. We can see the necessity for a separate approach, as the non-degenerate expression for the first correction to the wavefunctions blows up for energy differences that are small or identically zero.

More concretely, the issue is that there is no way to choose a unique basis of eigenstates of the unperturbed system. Consider the Hydrogen Hamiltonian $\mathcal{H}^{(0)}$, with $\mathcal{H}^{(0)} |nlm\rangle = E_n^{(0)} |nlm\rangle$. Since the energy eigenvalues $E_n^{(0)}$ depends only on the $n$ quantum number, the vector $|nlm\rangle$ is an eigenvector with eigenvalue $E_n^{(0)}$ for all values $0 \leq l \leq n-1$ and $-l \leq m \leq l$, so we could reasonably choose any of these vectors to be part of a basis representation of the system.

The solution is to treat the unperturbed states as general linear combinations of the degenerate states and then diagonalise the Hamiltonian in the space $D$ of degenerate states so that the contributions to the corrections come from only one of these new states. This avoids any $E_n^{(0)} - E_k^{(0)} = 0$ cases (for $n \neq k$) by ensuring the off-diagonal contributions are zero. We can then use the formulae for non-degenerate perturbation theory as before.

Finding the corrected energies to first order amounts to diagonalising

$$(\mathcal{H}^{(0)} + V) |\psi_n^{(0)}\rangle = (E_n^{(0)} + E_n^{(1)}) |\psi^{(0)}\rangle .$$

However, since we know $\mathcal{H}^{(0)} |\psi_n^{(0)}\rangle = E_n^{(0)} |\psi_n^{(0)}\rangle$, the corrections to the unperturbed energies are found from

$$V |\psi_n^{(0)}\rangle = E_n^{(1)} |\psi_n^{(0)}\rangle \implies E_n^{(1)} = \langle\psi_n^{(0)}| \widetilde{V} |\psi_n^{(0)}\rangle := \widetilde{V}_{nn}$$

where $\widetilde{V}_{nn}$ are the diagonal entries of the diagonalised matrix $\widetilde{V}_{nm} = \langle\psi_n^{(0)}| V |\psi_m^{(0)}\rangle$ in the new diagonal basis.

The first corrections to the wavefunctions are similar to the non-degenerate case

$$|\psi_n^{(1)}\rangle = \sum_{m \notin D} \frac{\langle\psi_m^{(0)}| V |\psi_n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}} |\psi_m^{(0)}\rangle .$$

## 3.3 The Linear Stark Effect

The linear Stark effect involves an external electric field acting on, e.g. a Hydrogen atom. The unperturbed energies are degenerate, as they depend on the $n$ quantum number and not on $l$ and $m$ quantum numbers. For a given state $|nlm\rangle$, we have $0 \leq l \leq n-1$ and $-l \leq m \leq l$. For example, the $n = 2$ state has

2s singlet state: $l = 0, m = 0$

2p triplet state: $l = 1, m = -1, 0, 1$

This $n = 2$ state is four-fold degenerate, with each of the four states having energy $E_{n=2} = -\dfrac{q_e^2}{8a_0}$.

Applying an external electric field perturbs the system such that

$$\mathcal{H} = \mathcal{H}^{(0)} - e|\vec{E}_{\text{ext}}|\hat{z}.$$

In the case of $n = 2$, we want the diagonalised matrix $\widetilde{V}$ in the degenerate subspace ($n = 2$) whose matrix elements are $\langle l'm'| V |lm\rangle$. Noting that

$$[L_z, V] = -e|\vec{E}_{\text{ext}}|[L_z, \hat{z}] = 0,$$

we see that $\langle l'm'| [L_z, V] |lm\rangle = 0$ which implies that $\langle l'm'| V |lm\rangle = 0$ for $m \neq m'$. That is, $|lm\rangle$ is a "good" basis of eigenstates; one that diagonalises $\widetilde{V}$. We can compute these matrix elements using the eigenstates of Hydrogen

$$\psi_{200} = \frac{1}{\sqrt{4\pi}} \left(\frac{1}{2a_0}\right)^{3/2} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0},$$

$$\psi_{210} = \frac{1}{\sqrt{4\pi}} \left(\frac{1}{2a_0}\right)^{3/2} \frac{r}{a_0} e^{-r/2a_0} \cos\theta.$$

We find that

$$\langle 00| V |10\rangle = \langle 10| V |00\rangle = \int d^3\vec{r} \psi^*_{200}(\vec{r})(-e|\vec{E}_{\text{ext}}|\hat{z}\psi_{210}(\vec{r}) = 3ea_0|\vec{E}_{\text{ext}}|.$$

So, the eigenvalues of $\widetilde{V}$ are

$$\Delta^{(1)}_{\pm} = \pm 3ea_0|\vec{E}_{\text{ext}}|, 0, 0$$

and the corrected states are

$$|\pm\rangle = \frac{1}{\sqrt{2}} \left(|00\rangle \mp |10\rangle\right).$$

The fine structure of Hydrogen has contributions from relativistic effects and spin-orbit coupling, but both of these effects are smaller by a factor of $\alpha = \frac{q_e^2}{4\pi\varepsilon_0 \hbar c}$, the fine-structure constant. The fine-structure constant actually gets its name from its introduction by Arnold Sommerfeld in 1916 to quantify the fine structure of spectral lines of the Hydrogen atom, which had been accurately measured by Michelson and Morley.

## 3.4 Variational Method

**Theorem:**
*Given any properly normalised state $|\Psi\rangle$, the ground state energy $E_g$ of a system with Hamiltonian $\mathcal{H}$ is bounded by the expectation value of the Hamiltonian with respect to the state $|\Psi\rangle$. That is,*

$$E_g \leq \langle\Psi| \mathcal{H} |\Psi\rangle := \langle\mathcal{H}\rangle.$$

**Proof:**
Let $|\psi_n\rangle$ be the eigenfunctions of $\mathcal{H}$, i.e. $\mathcal{H}|\psi_n\rangle = E_n |\psi_n\rangle$, which form a basis such that for some state $|\Psi\rangle$,

$$|\Psi\rangle = \sum_n c_n |\psi_n\rangle.$$

Requiring that $|\psi_n\rangle$ and $|\Psi\rangle$ are properly normalised, we have

$$\langle\Psi|\Psi\rangle = 1 = \sum_n c_n^* c_n \langle\psi_n|\psi_n\rangle = \sum_n |c_n|^2.$$

We also see that

$$\langle\mathcal{H}\rangle = \langle\Psi| \mathcal{H} |\Psi\rangle = \sum_n \langle\psi_n| c_n^* \mathcal{H} c_n |\psi_n\rangle = \sum_n |c_n|^2 \langle\psi_n| E_n |\psi_n\rangle = \sum_n |c_n|^2 E_n.$$

We know, however, that the ground state energy is the lowest energy, i.e. $E_n \geq E_g$. Thus,

$$\langle\mathcal{H}\rangle = \sum_n |c_n|^2 E_n \geq \sum_n |c_n|^2 E_g = E_g \sum_n |c_n|^2 = E_g,$$

which is our required result

$$\langle\mathcal{H}\rangle \geq E_g.$$

This method can be used to estimate the ground state energy of a system when an analytic solution may not exist. For examples, as well as a similar proof for the first excited energy, see Homework 3.

# 4 Time-Dependent Perturbation Theory

## 4.1 Two-Level Systems

Often we want to study systems experiencing an external effect which is time dependent, such as an alternating electric field, which can change which states are occupied in the system. We first consider a two-level system such that

$$\mathcal{H}^{(0)}\left|\psi_1\right\rangle = E_1\left|\psi_2\right\rangle,$$

$$\mathcal{H}^{(0)}\left|\psi_2\right\rangle = E_2\left|\psi_2\right\rangle.$$

In the Schrödinger picture, the time evolution of states is governed by the Schrödinger equation:

$$i\hbar\frac{\partial|\psi(t)\rangle}{\partial t} = \mathcal{H}\left|\psi(t)\right\rangle$$

where $\mathcal{H} = \mathcal{H}^{(0)} + \mathcal{H}'$. Given the initial condition $|\psi(0)\rangle = c_1\left|\psi_1\right\rangle + c_2\left|\psi_2\right\rangle$ such that $|c_1|^2 + |c_2|^2 = 1$, then for $\mathcal{H}' = 0$ (and time-independent $\mathcal{H}^{(0)}$), the state evolution is

$$|\psi(t)\rangle = c_1 e^{-iE_1 t/\hbar}\left|\psi_1\right\rangle + c_2 e^{-iE_2 t/\hbar}\left|\psi_2\right\rangle.$$

When the perturbation is applied, $\mathcal{H}' \neq 0$ and the quantities $c_1$ and $c_2$ will generally be time dependent. Defining the quantities $\mathcal{H}'_{ij} = \left\langle\psi_i\right|\mathcal{H}'\left|\psi_j\right\rangle$ and $\hbar\omega_0 = E_2 - E_1$, the Schrödinger equation gives coupled differential equations for $c_1(t)$ and $c_2(t)$.

$$\dot{c}_1(t) = -\frac{i}{\hbar}\left[c_1(t)\mathcal{H}'_{11} + c_2(t)\mathcal{H}'_{12}e^{-i\omega_0 t}\right],$$

$$\dot{c}_1(t) = -\frac{i}{\hbar}\left[c_2(t)\mathcal{H}'_{22} + c_1(t)\mathcal{H}'_{21}e^{i\omega_0 t}\right].$$

Assuming that $\mathcal{H}' << 1$ and that at $t = 0$ the system is in state 1, i.e. $c_1(0) = 1, c_2(0) = 0$, then we expand in orders of $\varepsilon << 1$, which controls the size of the perturbation.

$$c_1(t) = 1 + \varepsilon\tilde{c}_1(t) + \varepsilon^2\tilde{\tilde{c}}_1(t) + ...$$

$$c_1(t) = 0 + \varepsilon\tilde{c}_2(t) + \varepsilon^2\tilde{\tilde{c}}_2(t) + ...$$

Substituting this ansatz into the coupled differential equations, we get

$$\dot{\tilde{c}}_1(t) = 0 + \mathcal{O}(\varepsilon^2),$$

$$\dot{\tilde{c}}_2(t) = -\frac{i}{\hbar}\mathcal{H}'_{21}e^{i\omega_0 t} + \mathcal{O}(\varepsilon^2).$$

The second equation implies that

$$\tilde{c}_2(t) = -\frac{i}{\hbar}\int_0^t \mathcal{H}'_{21}e^{i\omega_0 t'}dt'.$$

To the next order in $\varepsilon$, we have

$$\dot{\tilde{\tilde{c}}}_1 = -\frac{i}{\hbar}\left(-\frac{i}{\hbar}\int_0^t \mathcal{H}'_{21}e^{i\omega_0 t'}dt'\right)\mathcal{H}'_{12}e^{-i\omega_0 t} + \mathcal{O}(\varepsilon^3)$$

$$\dot{\tilde{\tilde{c}}}_2 = 0 + \mathcal{O}(\varepsilon^3)$$

Grouping these together, we have (remembering that $\mathcal{H}'_{ij}$ is of order $\mathcal{O}(\varepsilon)$),

$$c_1(t) = 1 - \frac{i}{\hbar}\int_0^t dt'\left(\int_0^{t'} dt''\mathcal{H}'_{21}e^{i\omega_0 t}\right)\mathcal{H}'_{12}e^{-i\omega_0 t} + \mathcal{O}(\varepsilon^3),$$

$$c_2(t) = 0 - \frac{i}{\hbar}\int_0^t dt' \mathcal{H}'_{21} e^{i\omega_0 t} + \mathcal{O}(\varepsilon^3).$$

Remember that at time $t = 0$ the system is in state 1. The probability of finding the system in state 2 at some time $t > 0$ is

$$\mathcal{P}_{1\to 2}(t) = |c_2(t)|^2 \simeq \left| -\frac{i}{\hbar}\int_0^t dt' \mathcal{H}'_{21} e^{i\omega_0 t} \right|^2 .$$

## 4.2 Pictures of Quantum Mechanics

In the Schrödinger picture, which has been used up to now, it is the states that evolve according to the Schrödinger equation of motion

$$i\hbar \frac{\partial |\psi(t)\rangle}{\partial t} = \mathcal{H}(t)\left|\psi(t)\right\rangle .$$

This evolution in time can be expressed in an aptly named "time evolution operator", $T(t, t_0)$, which satisfies (or rather is defined by) the equation

$$i\hbar \frac{dT(t,t_0)}{dt} = \mathcal{H}(t) T(t, t_0),$$

with $T(t_0, t_0) = \mathbb{1}$, to get

$$\left|\psi(t)\right\rangle = T(t,t_0)\left|\psi(t_0)\right\rangle .$$

In the case where the Hamiltonian is time-independent, we can write it as

$$T(t, t_0) = \exp\left(-\frac{i}{\hbar}(t - t_0)\mathcal{H}\right).$$

When we study systems we do so by making measurements, and these measurements correspond to observables which correspond to operators (the measured values correspond to the eigenvalues of operators), so it is reasonable to suggest shifting all of the time dependence from the states onto the operators themselves. Instead of thinking of the states changing in time and then making fixed measurements on them, we think of the measurements we can make on those states being time dependent. This is the Heisenberg picture.

We can define a time-dependent operator $\hat{A}(t)$ by transforming a Schrödinger picture operator

$$\hat{A}(t) = T^\dagger(t, t_0)\hat{A}T(t, t_0),$$

which satisfies the Heisenberg equation of motion

$$i\hbar \frac{d\hat{A}(t)}{dt} = [\hat{A}(t), \mathcal{H}(t)].$$

A third picture is what's called the Dirac, or interaction picture. In this picture, both the states and operators carry some of the time dependence of the system. The key advantage is that the Hamiltonian is split into a "free part" which is usually known and solvable, and an "interaction part" which represents an interaction with or perturbation on the known system;

$$\mathcal{H} = \mathcal{H}_0 + V.$$

We can define an evolution operator

$$\mathcal{U}(t) = T_{\mathcal{H}_0}(0, t) = T^\dagger_{\mathcal{H}_0}(t, 0),$$

which satisfies $\mathcal{U}(0) = \mathbb{1}$ and satisfies the equation of motion

$$i\hbar \frac{d\mathcal{U}(t)}{dt} = -\mathcal{U}(t)\mathcal{H}_0.$$

Note that if $\mathcal{H}_0$ is time-independent, we can write $\mathcal{U}(t)$ explicitly as

$$\mathcal{U}(t) = \exp\left(-\frac{i}{\hbar}\mathcal{H}_0 t\right).$$

This will become useful soon! We can use this evolution operator to define an interaction picture operator

$$\widetilde{A}(t) = \mathcal{U}(t) A \mathcal{U}^\dagger(t)$$

satisfying the equation of motion

$$i\hbar\frac{d\widetilde{A}(t)}{dt} = [\widetilde{A}(t), \widetilde{\mathcal{H}}_0],$$

where $\widetilde{\mathcal{H}}_0 = \mathcal{U}(t)\mathcal{H}_0\mathcal{U}^\dagger(t)$.

The interaction picture states are defined in terms of the Schrödinger picture states

$$|\widetilde{\psi}(t)\rangle = \mathcal{U}(t)\,|\psi(t)\rangle$$

and satisfy the interaction picture equation of motion

$$i\hbar\frac{d\,|\widetilde{\psi}(t)\rangle}{dt} = \widetilde{V}\,|\widetilde{\psi}(t)\rangle$$

where $\widetilde{V} = \mathcal{U}(t)V\mathcal{U}^\dagger(t)$. Notice the similarity in all these equations of motion, especially between the Schrödinger picture equation and the interaction picture equation. In a similar way to how we defined the time evolution operator $T(t, t_0)$ in the Schrödinger picture, we can define the interaction picture time evolution operator such that

$$|\widetilde{\psi}(t)\rangle = \widetilde{T}(t, t_0)\,|\widetilde{\psi}(t_0)\rangle$$

satisfying the equation

$$i\hbar\frac{d\widetilde{T}(t, t_0)}{dt} = \widetilde{V}(t)\widetilde{T}(t, t_0), \quad \widetilde{T}(t_0, t_0) = \mathbb{1}.$$

## 4.3 The Dyson Series

We now consider the case where the free Hamiltonian $\mathcal{H}_0$ is time-independent and its energy eigenvalues and eigenstates are known. We can integrate our expression for the interaction picture time evolution operator.

$$\widetilde{T}(t, t_0) = \mathbb{1} - \frac{i}{\hbar}\int_{t_0}^{t}\widetilde{V}(t_1)\widetilde{T}(t_1, t_0)dt_1.$$

If we continue to substitute this expression for $\widetilde{T}(t, t_0)$ into itself, we get repeated nested integrals

$$\widetilde{T}(t, t_0) = \mathbb{1} + \sum_{n=1}^{\infty}\left(\frac{-i}{\hbar}\right)^n \int_{t_0}^{t} dt_1 \cdots \int_{t_0}^{t_{n-1}} dt_n \widetilde{V}(t_1)\cdots\widetilde{V}(t_n).$$

We can see that the potentials are ordered in decreasing time. Introducing a time ordering operator $\mathbb{T}[\cdots]$, which orders terms with later/larger times on the left. This results in a time-ordered exponential solution called the Dyson Series

$$\widetilde{T}(t, t_0) = \mathrm{Texp}\left(-\frac{i}{\hbar}\int_{t_0}^{t}\widetilde{V}(t')dt'\right).$$

This is most useful when the interaction potential $\widetilde{V}$ is small, so that only the first few terms need to be considered.

## 4.4 Time-Dependent Perturbations

Now that we have an expression for the interaction picture time evolution operator, we'll consider the case where $\mathcal{H}_0$ is time-independent, with energies $E_n$ and eigenstates $|n\rangle$. We can ask ourselves, what's the probability to find our system in a state $|n\rangle$ at some time $t$ if it is in a state $|m\rangle$ at time $t_0$?

What we are essentially asking is what is the overlap of the states $|n\rangle$ and $|m\rangle$ at time $t$? First, we have to evolve the state $|m\rangle$ forward in time from $t_0$. This is just acting with $\widetilde{T}(t,t_0)$! Thus, at time $t$ the system is in the state $\widetilde{T}(t,t_0)\,|m\rangle$. The overlap of this state with the state $|n\rangle$ is the transition amplitude

$$C_{nm}(t) = \langle n|\,\widetilde{T}(t,t_0)\,|m\rangle$$

which is just the $n,m$ matrix element of the operator $\widetilde{T}(t,t_0)$. Expanding the Dyson Series up to first order, we get a first order expression for these transition amplitudes

$$C_{nm}(t) = \langle n|m\rangle - \frac{i}{\hbar}\int_{t_0}^{t} dt'\,\langle n|\,\widetilde{V}(t')\,|m\rangle\,.$$

Remember, however, that $\widetilde{V}(t) = \mathcal{U}(t)V\mathcal{U}^\dagger(t)$ and we have an explicit expression for $\mathcal{U}(t)$ when $\mathcal{H}_0$ is time independent. Thus,

$$\langle n|\,\widetilde{V}(t)\,|m\rangle = \langle n|\,e^{i\mathcal{H}_0 t/\hbar}Ve^{-i\mathcal{H}_0 t/\hbar}\,|m\rangle = \langle n|\,e^{iE_n t/\hbar}Ve^{-iE_m t/\hbar}\,|m\rangle = e^{i\omega_{nm}t}V_{nm},$$

where we have defined $\hbar\omega_{nm} = E_n - E_m$ and $V_{nm} = \langle n|\,V\,|m\rangle$. Thus, to first order the transition amplitude is

$$C_{nm}(t) = \delta_{nm} - \frac{i}{\hbar}\int_{t_0}^{t} dt' e^{i\omega_{nm}t'}V_{nm}(t').$$

The probability of finding the system in the state $|n\rangle$, $n \neq m$, at time $t$ is

$$\mathcal{P}_{m\to n}(t) = |C_{nm}(t)|^2 \simeq \left|-\frac{i}{\hbar}\int_{t_0}^{t} dt' e^{i\omega_{nm}t'}V_{nm}(t')\right|^2.$$

## 4.5 Density of States and Fermi's Golden Rule

If the interaction potential $V(t) = 0$ for $t \leq 0$ and a constant $V(t) = V$ for $t > 0$, then the transition amplitude will be

$$C_{nm} = \frac{-i}{\hbar}V_{nm}\int_{0}^{t} dt' e^{i\omega_{nm}t'} = \frac{-i}{\hbar}\frac{V_{nm}}{\omega_{nm}}\left(1 - e^{i\omega_{nm}t}\right).$$

The transition probability between the initial state $|m\rangle$ and the final state $|n\rangle$ is then

$$\mathcal{P}_{m\to n}(t) = |C_{nm}|^2 = \frac{4|V_{nm}|^2}{(E_n - E_m)^2}\sin^2\left(\frac{\omega_{nm}t}{2}\right).$$

Note that the quantities $C_{nm}(t)$ and $\mathcal{P}_{m\to n}(t)$ are assumed to remain small, otherwise the interaction will be large, which falls outside the scope of perturbation theory. Thus, $\mathcal{P}_{m\to m} \approx 1$.

If there are a large number of states with energies close to $E_m$, it's useful to introduce a density of states $\rho(E)$, where $\rho(E)dE$ is the number of states with energies between $E$ and $E + dE$. The sum of the transition probabilities from the state with energy $E_m$ into states with energies near $E_m$ can be approximated by an integral

$$\sum_{\{n\}}\mathcal{P}_{m\to n}(t) \simeq \int_{\Delta E} dE_n\rho(E_n)\mathcal{P}_{m\to n}(t).$$

Assuming that $\rho(E_n)$ and $V_{nm}$ are constant over the range $\Delta E$, this can be written as

$$\sum_{\{n\}} \mathcal{P}_{m\to n}(t) = 4\rho(E_m)|V_{nm}|^2 \int dE_n \frac{\sin^2\left(\frac{(E_n-E_m)t}{2\hbar}\right)}{(E_n-E_m)^2}.$$

Computing this integral using the delta function definition $\lim\limits_{\alpha\to\infty} \dfrac{1}{\pi}\dfrac{\sin^2(\alpha x)}{\alpha x^2} = \delta(x)$, we get

$$\sum_{\{n\}} \mathcal{P}_{m\to n}(t) \simeq \frac{2\pi\rho(E_m)}{\hbar}|V_{nm}|^2 t.$$

The "probability transition rate" is defined as

$$w_{m\to\{n\}} := \frac{d}{dt}\sum_{\{n\}} \mathcal{P}_{m\to n}(t) = \frac{2\pi}{\hbar}|V_{nm}|^2\rho(E_m).$$

This is Fermi's Golden Rule.

# 5 Scattering

## 5.1 Scattering Cross Section

In the case of quantum scattering (off a spherically symmetric potential), our interaction picture time evolution operator takes plane wave states $\left|\vec{k}\right\rangle$ from infinity (at $t_0 \to -\infty$) and expresses them as spherical waves at time $t$ that have hit the potential and scattered away. Since we are taking the limit $t_0 \to -\infty$, we add a convergence factor so that the quantity

$$\langle n|\,\widetilde{T}(t,-\infty)\,|m\rangle = \delta_{nm} - \frac{i}{\hbar}T_{nm}\int_{-\infty}^{t} e^{i\omega_{nm}t'+\varepsilon t'}dt'$$

reduces to the usual expression in terms of $V_{nm}$ as $\varepsilon \to 0$. We can also define a scattering matrix which describes the transformation between the initial states at $t_0 \to -\infty$ and the final states at $t \to \infty$ as

$$\mathcal{S}_{nm} := \lim_{t\to\infty}\lim_{\varepsilon\to 0}\langle n|\,\widetilde{T}(t,-\infty)\,|m\rangle = \delta_{nm} - 2\pi i\delta(E_n-E_m)T_{nm}.$$

Just as with time-dependent perturbation theory, we can use these to find a probability transition rate

$$w_{m\to n} = \frac{2\pi}{\hbar}|T_{nm}|^2\delta(E_n-E_m).$$

Our indident plane waves have energy $E_{\vec{n}} = \dfrac{\hbar^2}{2m}\left(\dfrac{2\pi}{L}\right)^2|\vec{n}|$, where $L$ is the side length of a "box" where the particles exist (which is taken to infinity for the continuous case). The density of states is defined in terms of the density of states in some infinitesimal solid angle of a sphere.

$$\rho(E_n) = \lim_{\Delta E\to 0}\frac{\Delta N}{\Delta E} = \frac{4\pi|\vec{n}|^2\Delta|\vec{n}|\dfrac{d\Omega_f}{4\pi}}{\dfrac{\hbar^2}{2m}\dfrac{2\pi}{L}|\vec{n}|2\Delta|\vec{n}|} = \frac{mk_f}{\hbar^2}\left(\frac{L}{2\pi}\right)^3 d\Omega_f,$$

where $d\Omega_f$ is the solid angle through which we are looking for scattered waves and $k_f$ is the magnitude of the final, outgoing wavevector. For elastic scattering, the incident and final energies are equal; $E_i = E_f$ and so the incident and final wavevectors are equal in magnitude; $k_i = k_f$. Thus, the probability transition rate is

$$w_{i\to f} = \frac{mk_iL^3}{(2\pi)^2\hbar^3}|T_{fi}|^2 d\Omega_f.$$

The scattering cross section $d\sigma$ is the transition rate per unit incoming flux. The incoming flux $\vec{j} = \frac{\hbar}{m}\frac{\vec{k}}{L^3}$, so we have a differential cross section

$$\frac{d\sigma}{d\Omega_f} = \frac{mL^3}{2\pi\hbar^2}|T_{fi}|^2.$$

## 5.2 Scattering Amplitudes

The Lippmann-Schwinger equation

$$|\psi^{(+)}\rangle = |m\rangle + \frac{1}{E_m - \mathcal{H}_0 + i\hbar\varepsilon} V\,|\psi^{(+)}\rangle\,,$$

which can be found from considering the matrix elements of $T_{nm}$, gives the state vector for the scattering system. In its position space representation, it leads to a Green's function which is the Green's function of the Helmholtz equation $(\nabla^2 + k^2)G_\pm(\vec{x},\vec{x}') = \delta^{(3)}(\vec{x}-\vec{x}')$. Namely, we find

$$\psi^{(+)}(\vec{x}) = \psi_0(\vec{x}) - \frac{2m}{\hbar^2}\int d^3\vec{x}'\,\frac{e^{ik|\vec{x}-\vec{x}'|}}{4\pi|\vec{x}-\vec{x}'|}V(\vec{x}')\psi^{(+)}(\vec{x}').$$

Far from the origin, $|\vec{x}-\vec{x}'| \simeq r - \hat{r}\cdot\vec{x}'$, so the state vector becomes

$$\psi^{(+)}(\vec{x}) \to \psi_k(\vec{x}) + \frac{e^{ikr}}{r}\left(-\frac{m}{2\pi\hbar^2}\right)\int d^3\vec{x}' e^{-i\vec{k}'\cdot\vec{x}'}V(\vec{x}')\psi^{(+)}(\vec{x}') := \frac{1}{L^{3/2}}\left[e^{i\vec{k}\cdot\vec{x}} + \frac{e^{ikr}}{r}f(\vec{k}',\vec{k})\right],$$

where $f(\vec{k}',\vec{k})$ is the scattering amplitude which depends on the incoming and outgoing wavevectors. We see now that the wave vector describing the total system is the superposition of a plane wave and a spherical wave, modulated by an amplitude factor which depends on the direction. Noting that $f(\vec{k}',\vec{k}) = \frac{mL^3}{2\pi\hbar^2}\left\langle\vec{k}'\right| V\,|\psi^{(+)}\rangle$, which implies that

$$\frac{d\sigma}{d\Omega} = |f(\vec{k}',\vec{k})|^2.$$

To a first order approximation, by taking $\psi^{(+)}$ to be a plane wave, we have

$$f^{(1)}(\vec{k}',\vec{k}) = -\frac{m}{2\pi\hbar^2}\int d^3\vec{x}' e^{-i(\vec{k}'-\vec{k})\cdot\vec{x}'}V(\vec{x}').$$

This is called the First Born Approximation. Defining the momentum transfer $\vec{q} = \vec{k} - \vec{k}'$ and assuming a spherically symmetric potential $V(\vec{x}') = V(r')$, we get

$$f^{(1)}(\vec{k}',\vec{k}) = -\frac{2m}{q\hbar^2}\int_0^\infty r\,dr\,V(r)\sin(qr).$$