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5.74 Introductory Quantum Mechanics II
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5.74 TIME-DEPENDENT QUANTUM MECHANICS

1. INTRODUCTION

1.1. Time-evolution for time-independent Hamiltonians

The time evolution of the state of a quantum system is described by the time-dependent Schrödinger equation (TDSE):

$$i\hbar \frac{\partial}{\partial t} \psi(\vec{r}, t) = \hat{H} \psi(\vec{r}, t) \quad (1.1)$$

\hat{H} is the Hamiltonian operator which describes all interactions between particles and fields, and is the sum of the kinetic and potential energy. For one particle

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}, t) \quad (1.2)$$

The state of the system is expressed through the wavefunction $\psi(\vec{r}, t)$. The wavefunction is complex and cannot be observed itself, but through it we obtain the probability density

$$P = \int \psi^*(\vec{r}, t) \psi(\vec{r}, t) d\vec{r} = \langle \psi(\vec{r}, t) | \psi(\vec{r}, t) \rangle \quad (1.3)$$

which characterizes the probability that the particle described by \hat{H} is between \vec{r} and $d\vec{r}$ at time t .

Most of what you have previously covered is time-independent quantum mechanics, where we mean that the Hamiltonian \hat{H} is assumed to be independent of time: $\hat{H} = \hat{H}(\vec{r})$. We then assume a solution with a form in which the spatial and temporal variables in the wavefunction are separable:

$$\psi(\vec{r}, t) = \varphi(\vec{r}) T(t) \quad (1.4)$$

$$i\hbar \frac{1}{T(t)} \frac{\partial}{\partial t} T(t) = \frac{\hat{H}(\vec{r}) \varphi(\vec{r})}{\varphi(\vec{r})} \quad (1.5)$$

Here the left-hand side is a function only of time (t), and the right-hand side is a function of space only (\vec{r} , or rather position and momentum). Equation (1.5) can only be satisfied if both sides are equal to the same constant, E . Taking the right hand side we have

$$\frac{\hat{H}(\vec{r})\varphi(\vec{r})}{\varphi(\vec{r})} = E \quad \Rightarrow \quad \hat{H}(\vec{r})\varphi(\vec{r}) = E\varphi(\vec{r}) \quad (1.6)$$

This is our beloved Time-Independent Schrödinger Equation (TISE). The TISE is an eigenvalue equation, for which $\varphi(\vec{r})$ are the eigenstates and E is the eigenvalue. Here we note that $\langle \hat{H} \rangle = \langle \psi | \hat{H} | \psi \rangle = E$, so \hat{H} is the operator corresponding to E and drawing on classical mechanics we associate $\langle \hat{H} \rangle$ with the expectation value of the energy of the system. Now taking the left hand side of (1.5):

$$i\hbar \frac{1}{T(t)} \frac{\partial T}{\partial t} = E \quad \Rightarrow \quad \left(\frac{\partial}{\partial t} + \frac{iE}{\hbar} \right) T(t) = 0 \quad (1.7)$$

$$T(t) = T_0 \exp(-iEt / \hbar) = T_0 \exp(-i\omega t) \quad (1.8)$$

So, in the case of a bound potential we will have a discrete set of eigenfunctions $\varphi_n(\vec{r})$ with corresponding energy eigenvalues E_n from the TISE, and there are a set of corresponding solutions to the TDSE.

$$\psi_n(\vec{r}, t) = c_n \varphi_n(\vec{r}) \exp(-i\omega_n t) \quad (1.9)$$

where $\omega_n = E_n / \hbar$ and c_n is a (complex) amplitude. The n eigenfunctions form an orthonormal set, so that $\sum_n |c_n|^2 = 1$. Since the only time-dependence is a phase factor, the probability density (1.3) is independent of time for the eigenfunctions $\psi_n(\vec{r}, t)$. Therefore, the eigenstates $\varphi(\vec{r})$ do not change with time and are called **stationary states**.

However, more generally, a system may exist as a linear combination of eigenstates:

$$\psi(\vec{r}, t) = \sum_n c_n \psi_n(\vec{r}, t) = \sum_n c_n e^{-i\omega_n t} \phi_n(\vec{r}) \quad (1.10)$$

where c_n are (complex) amplitudes. For such a case, the probability density will oscillate with time. As an example, consider two eigenstates

$$\psi(\vec{r}, t) = \psi_1 + \psi_2 = c_1 \phi_1 e^{-i\omega_1 t} + c_2 \phi_2 e^{-i\omega_2 t} \quad (1.11)$$

For this state the probability density oscillates in time as $\cos(\omega_2 - \omega_1)t$:

$$\begin{aligned} P(t) &= |\psi|^2 = |\psi_1 + \psi_2|^2 \\ &= |\psi_1|^2 + |\psi_2|^2 + 2 \operatorname{Re}[\psi_1^* \psi_2] \\ &= |c_1 \phi_1|^2 + |c_2 \phi_2|^2 + c_1^* c_2 \phi_1^* \phi_2 e^{-i(\omega_2 - \omega_1)t} + c_2^* c_1 \phi_2^* \phi_1 e^{+i(\omega_2 - \omega_1)t} \\ &= |\psi_1|^2 + |\psi_2|^2 + 2|\psi_1||\psi_2|\cos(\omega_2 - \omega_1)t \end{aligned} \quad (1.12)$$

We refer to this as a **coherence**, a coherent superposition state. If we include momentum (a wavevector) of particle associated with this state, we often describe this as a wavepacket.

Time Evolution Operator

More generally, we want to understand how the wavefunction evolves with time. The TDSE is linear in time. Since the TDSE is deterministic, we will define an operator that describes the dynamics of the system:

$$\psi(t) = \hat{U}(t, t_0) \psi(t_0) \quad (1.13)$$

U is a propagator that evolves the quantum system as a function of time. For the **time-independent Hamiltonian**:

$$\frac{\partial}{\partial t} \psi(\vec{r}, t) + \frac{i\hat{H}}{\hbar} \psi(\vec{r}, t) = 0 \quad (1.14)$$

To solve this, we will define an operator $\hat{T} = \exp(-i\hat{H}t / \hbar)$, which is a **function of an operator**.

A function of an operator is defined through its expansion in a Taylor series:

$$\begin{aligned}\hat{T} &= \exp(-i\hat{H}t/\hbar) = 1 - \frac{i\hat{H}t}{\hbar} + \frac{1}{2!} \left(\frac{i\hat{H}t}{\hbar} \right)^2 - \dots \\ &= f(\hat{H})\end{aligned}\tag{1.15}$$

Note: about functions of an operator \hat{A} : Given a set of eigenvalues and eigenvectors of \hat{A} , i.e., $\hat{A}\varphi_n = a_n\varphi_n$, you can show by expanding the function as a polynomial that $f(\hat{A})\varphi_n = f(a_n)\varphi_n$

You can also confirm from the expansion that $\hat{T}^{-1} = \exp(i\hat{H}t/\hbar)$, noting that \hat{H} is Hermetian and \hat{H} commutes with \hat{T} . Multiplying eq. (1.14) from the left by \hat{T}^{-1} , we can write

$$\frac{\partial}{\partial t} \left[\exp\left(\frac{i\hat{H}t}{\hbar}\right) \psi(\bar{r}, t) \right] = 0,\tag{1.16}$$

and integrating $t_0 \rightarrow t$, we get

$$\exp\left(\frac{i\hat{H}t}{\hbar}\right) \psi(\bar{r}, t) - \exp\left(\frac{i\hat{H}t_0}{\hbar}\right) \psi(\bar{r}, t_0) = 0\tag{1.17}$$

$$\psi(\bar{r}, t) = \exp\left(\frac{-\hat{H}(t-t_0)}{\hbar}\right) \psi(\bar{r}, t_0)\tag{1.18}$$

So, we see that the time-propagator is

$$\hat{U}(t, t_0) = \exp\left(\frac{-\hat{H}(t-t_0)}{\hbar}\right),\tag{1.19}$$

and therefore

$$\psi_n(\bar{r}, t) = e^{-E_n(t-t_0)/\hbar} \psi_n(\bar{r}, t_0).\tag{1.20}$$

In which I have used the definition of the exponential operator for $e^{-i\hat{H}t/\hbar}|\varphi_n\rangle = e^{-iE_n t/\hbar}|\varphi_n\rangle$.

Alternatively, if we substitute the projection operator (or identity relationship)

$$\sum_n |\varphi_n\rangle\langle\varphi_n| = 1 \quad (1.21)$$

into eq. (1.19), we see

$$\begin{aligned} \hat{U}(t, t_0) &= e^{-i\hat{H}(t-t_0)/\hbar} \sum_n |\varphi_n\rangle\langle\varphi_n| \\ &= \sum_n e^{-i\omega_n(t-t_0)} |\varphi_n\rangle\langle\varphi_n|. \end{aligned} \quad \omega_n = \frac{E_n}{\hbar} \quad (1.22)$$

This form is useful when φ_n are characterized. So now we can write our time-developing wavefunction as

$$\begin{aligned} |\psi_n(\vec{r}, t)\rangle &= |\varphi_n\rangle \sum_n e^{-i\omega_n(t-t_0)} \langle\varphi_n|\psi_n(\vec{r}, t_0)\rangle \\ &= \sum_n e^{-i\omega_n(t-t_0)} c_n \\ &= \sum_n c_n(t) |\varphi_n\rangle \end{aligned} \quad (1.23)$$

As written in eq. (1.13), we see that the time-propagator $\hat{U}(t, t_0)$ acts to the right (on *kets*) to evolve the system in time. The evolution of the conjugate wavefunctions (*bras*) is under the Hermetian conjugate of $\hat{U}(t, t_0)$ acting to the left:

$$\langle\psi(t)| = \langle\psi(t_0)|\hat{U}^\dagger(t, t_0) \quad (1.24)$$

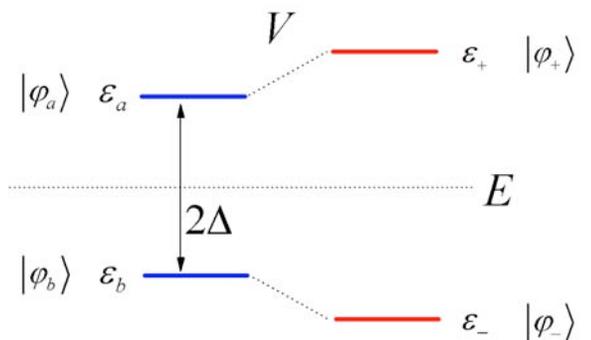
From its definition as an expansion and recognizing \hat{H} as Hermetian, you can see that

$$\hat{U}^\dagger(t, t_0) = \exp\left[\frac{i\hat{H}(t-t_0)}{\hbar}\right] \quad (1.25)$$

1.2. Time-evolution of a coupled two-level system (2LS)

Let's use this propagator using an example that we will refer to often. It is common to reduce or map quantum problems onto a 2LS. We will pick the most important states –the ones we care about– and then discard the remaining degrees of freedom, or incorporate them as a collection or continuum of other degrees of freedom termed a “bath”, $\hat{H} = \hat{H}_0 + \hat{H}_{bath}$.

We will discuss the time-evolution of a 2LS with a time-independent Hamiltonian. Consider a 2LS with two (unperturbed) states $|\varphi_a\rangle$ and $|\varphi_b\rangle$ with energies ε_a and ε_b , which are then coupled through an interaction V_{ab} . We will ask: If we prepare the system in state $|\varphi_a\rangle$, what is the time-dependent probability of observing it in $|\varphi_b\rangle$?

$$\begin{aligned} \hat{H} &= |\varphi_a\rangle \varepsilon_a \langle \varphi_a| + |\varphi_b\rangle \varepsilon_b \langle \varphi_b| \\ &\quad + |\varphi_a\rangle V_{ab} \langle \varphi_b| + |\varphi_b\rangle V_{ba} \langle \varphi_a| \\ &= \begin{pmatrix} \varepsilon_a & V_{ab} \\ V_{ba} & \varepsilon_b \end{pmatrix} \end{aligned} \quad (1.26)$$


The states $|\varphi_a\rangle$ and $|\varphi_b\rangle$ are in the uncoupled or noninteracting basis, and when we talk about spectroscopy these might refer to nuclear or electronic states in what I refer to as a “site” basis or “local” basis. The coupling V mixes these states, giving two eigenstates of \hat{H} , $|\varphi_+\rangle$ and $|\varphi_-\rangle$, with corresponding energy eigenvalues ε_+ and ε_- .

We start by searching for the eigenvalues and eigenfunctions of the Hamiltonian. Since the Hamiltonian is Hermetian, $(H_{ij} = H_{ji}^*)$, we write

$$V_{ab} = V_{ba}^* = V e^{-i\phi} \quad (1.27)$$

$$\hat{H} = \begin{pmatrix} \varepsilon_a & V e^{-i\phi} \\ V e^{+i\phi} & \varepsilon_b \end{pmatrix} \quad (1.28)$$

Now we define variables for the mean energy and energy splitting between the uncoupled states

$$E = \frac{\varepsilon_a + \varepsilon_b}{2} \quad (1.29)$$

$$\Delta = \frac{\varepsilon_a - \varepsilon_b}{2} \quad (1.30)$$

Then we obtain the eigenvalues of the coupled system by solving the secular equation

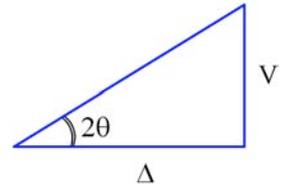
$$\det(H - \lambda I) = 0, \quad (1.31)$$

giving

$$\varepsilon_{\pm} = E \pm \sqrt{\Delta^2 + V^2} \quad (1.32)$$

Because the expressions get messy, we don't use this expression to find the eigenvectors for the coupled system, $|\varphi_{\pm}\rangle$. Rather, we use a substitution where we define:

$$\tan 2\theta = \frac{V}{\Delta} \quad (1.33)$$



with $0 \leq \theta \leq \pi/2$. Now,

$$\hat{H} = E \bar{I} + \Delta \begin{pmatrix} 1 & \tan 2\theta e^{-i\phi} \\ \tan 2\theta e^{+i\phi} & -1 \end{pmatrix}. \quad (1.34)$$

and we can express the eigenvalues as

$$\varepsilon_{\pm} = E \pm \Delta \sec 2\theta \quad (1.35)$$

We want to find the eigenstates of the Hamiltonian, $|\varphi_{\pm}\rangle$ from $\hat{H}|\varphi_{\pm}\rangle = \varepsilon_{\pm}|\varphi_{\pm}\rangle$ where e.g. $|\varphi_{+}\rangle = c_a|\varphi_a\rangle + c_b|\varphi_b\rangle$. This gives

$$\begin{aligned} |\varphi_{+}\rangle &= \cos\theta e^{-i\phi/2} |\varphi_a\rangle + \sin\theta e^{i\phi/2} |\varphi_b\rangle \\ |\varphi_{-}\rangle &= -\sin\theta e^{-i\phi/2} |\varphi_a\rangle + \cos\theta e^{i\phi/2} |\varphi_b\rangle \end{aligned} \quad (1.36)$$

Note that this basis is orthonormal (complete and orthogonal): $\langle \varphi_+ | \varphi_+ \rangle + \langle \varphi_- | \varphi_- \rangle = 1$.

Now, let's examine the expressions for the eigenstates in two limits:

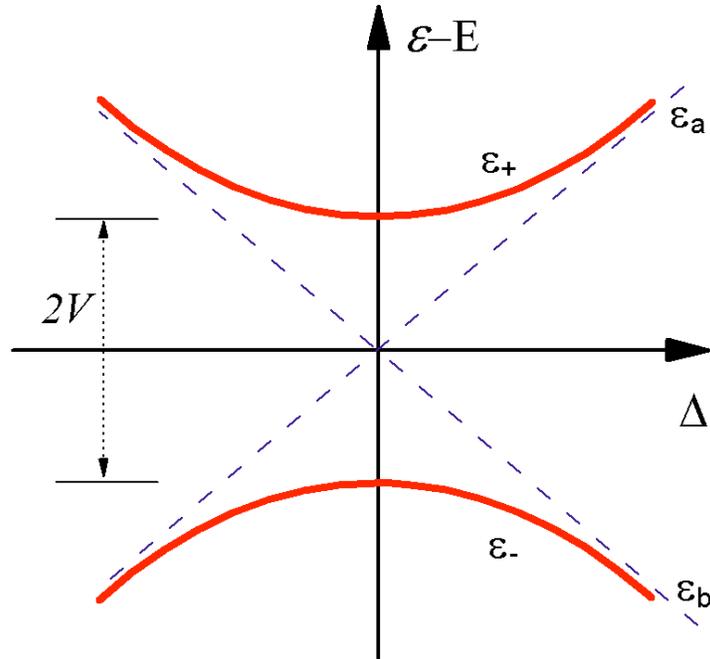
(a) Weak coupling ($V/\Delta \ll 1$). Here $\theta \approx 0$, and $|\varphi_+\rangle$ corresponds to $|\varphi_a\rangle$ weakly perturbed by the V_{ab} interaction. $|\varphi_-\rangle$ corresponds to $|\varphi_b\rangle$. In another way, as $\theta \rightarrow 0$, we find $|\varphi_+\rangle \rightarrow |\varphi_a\rangle$ and $|\varphi_-\rangle \rightarrow |\varphi_b\rangle$.

(b) Strong coupling ($V/\Delta \gg 1$). In this limit $\theta = \pi/4$, and the a/b basis states are indistinguishable. The eigenstates are symmetric and antisymmetric combinations:

$$|\varphi_{\pm}\rangle = \frac{1}{\sqrt{2}}(|\varphi_b\rangle \pm |\varphi_a\rangle) \quad (1.37)$$

Note from eq. (1.36) that the sign of V dictates whether $|\varphi_+\rangle$ or $|\varphi_-\rangle$ corresponds to the symmetric or antisymmetric combination. For negative $V \gg \Delta$, $\theta = -\pi/4$, and the correspondence changes.

We can schematically represent the energies of these states with the following diagram. Here we explore the range of ε_{\pm} available given a fixed value of the coupling V and a varying splitting Δ .



This diagram illustrates an avoided crossing effect. The strong coupling limit is equivalent to a degeneracy point ($\Delta \sim 0$) between the states $|\varphi_a\rangle$ and $|\varphi_b\rangle$. The eigenstates completely mix the unperturbed states, yet remain split by the strength of interaction $2V$. Such an avoided crossing is observed where two weakly interacting potential energy surfaces cross with one another at a particular nuclear displacement.

The time-evolution of this system is given by our time-evolution operator.

$$U(t, t_0) = |\varphi_+\rangle e^{-i\omega_+(t-t_0)} \langle\varphi_+| + |\varphi_-\rangle e^{-i\omega_-(t-t_0)} \langle\varphi_-| \quad (1.38)$$

where $\omega_{\pm} = \varepsilon_{\pm}/\hbar$. Since φ_a and φ_b are not the eigenstates, preparing the system in state φ_a will lead to time-evolution! Let's prepare the system so that it is initially in $|\varphi_a\rangle$.

$$(t_0 = 0) \quad |\psi(0)\rangle = |\varphi_a\rangle \quad (1.39)$$

What is the probability that it is found in state $|\varphi_b\rangle$ at time t ?

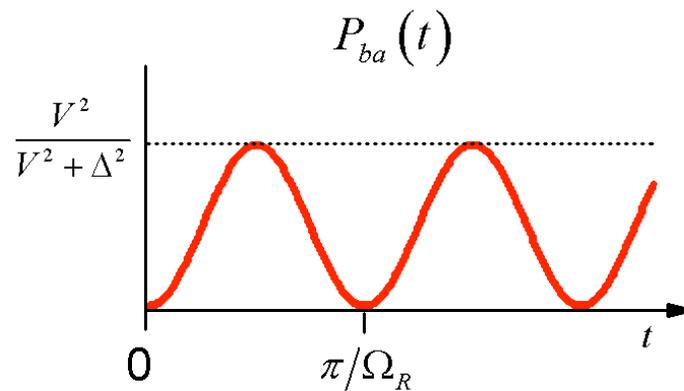
$$\begin{aligned} P_{ba}(t) &= \left| \langle\varphi_b|\psi(t)\rangle \right|^2 \\ &= \left| \langle\varphi_b|U(t, t_0)|\varphi_a\rangle \right|^2 \end{aligned} \quad (1.40)$$

To evaluate this, you need to know the transformation from the $|\varphi_a\rangle|\varphi_b\rangle$ basis to the $|\varphi_{\pm}\rangle$ basis, given in eq. (1.36). This leads to

$$P_{ba}(t) = \frac{V^2}{V^2 + \Delta^2} \sin^2 \Omega_R t \quad (1.41)$$

$$\Omega_R = \frac{1}{\hbar} \sqrt{\Delta^2 + V^2}. \quad (1.42)$$

Ω_R , the Rabi Frequency, represents the frequency at which probability amplitude oscillates between φ_a and φ_b states.



Notice for $V \rightarrow 0$, $\varphi_{\pm} \rightarrow \varphi_{a,b}$ (the stationary states), and there is no time-dependence.

For $V \gg \Delta$, then $\Omega_R = \frac{V}{\hbar}$ and $P = 1$ after $t = \frac{\pi}{2\Omega_R} = \frac{\hbar\pi}{2V}$.

Quantities we often calculate

Correlation amplitude: Measures the resemblance between the state of your system at time t and a target state $|\beta\rangle$:

$$C(t) = \langle \beta | \psi(t) \rangle \quad (1.43)$$

The probability amplitude $P(t) = |C(t)|^2$. If you express the initial state of your wavefunction in your eigenbasis $|\varphi_n\rangle$

$$|\psi(0)\rangle = \sum_n c_n |\varphi_n\rangle \quad (1.44)$$

$$\begin{aligned} C(t) &= \langle \beta | U(t, t_0) | \psi(0) \rangle \\ &= \sum_{m,n,j} c_m^* \langle \varphi_m | \varphi_j \rangle e^{-i\omega_j t} \langle \varphi_j | \varphi_n \rangle c_n \\ &= \sum_n c_m^* c_n e^{-i\omega_n t} \end{aligned} \quad (1.45)$$

Here c_m are the coefficients that project your target wavefunction $|\beta\rangle$ onto your eigenbasis. Note $\langle \varphi_m | \varphi_n \rangle = \delta_{nm}$.

Expectation values give the time-dependent average value of an operator. Physical observables correspond to the expectation values of Hermitian operators ($\hat{A} = \hat{A}^\dagger$), and therefore must be real. Expectation values of operators are given by

$$\begin{aligned} \langle \hat{A}(t) \rangle &= \langle \psi(t) | \hat{A} | \psi(t) \rangle \\ &= \langle \psi(0) | \hat{U}^\dagger(t, 0) \hat{A} \hat{U}(t, 0) | \psi(0) \rangle \end{aligned} \quad (1.46)$$

For an initial state $|\psi(0)\rangle = \sum_n c_n |\varphi_n\rangle$

$$\begin{aligned}
|\psi(t)\rangle &= \hat{U}(t,0)|\psi(0)\rangle = \sum_n e^{-i\omega_n t} c_n |\varphi_n\rangle = \sum_n c_n(t) |\varphi_n\rangle \\
\langle\psi(t)| &= \langle\psi(0)|\hat{U}^\dagger(t,0) = \sum_m e^{i\omega_m t} c_m^* \langle\varphi_m| = \sum_m c_m^*(t) \langle\varphi_m|
\end{aligned}
\tag{1.47}$$

$$\langle\hat{A}(t)\rangle = \sum_{m,n} c_n c_m^* e^{-i\omega_{nm} t} \langle\varphi_m|\hat{A}|\varphi_n\rangle = \sum_{m,n} c_n(t) c_m^*(t) A_{mn}
\tag{1.48}$$

$$\omega_{nm} = \frac{E_n - E_m}{\hbar} = \omega_n - \omega_m
\tag{1.49}$$

Note that for a Hermetian operator eq. (1.48) is real.

Readings

The material in this section draws from the following:

1. Cohen-Tannoudji, C.; Diu, B.; Lalöe, F. *Quantum Mechanics* (Wiley-Interscience, Paris, 1977) pp. 405-420.
2. Mukamel, S. *Principles of Nonlinear Optical Spectroscopy* (Oxford University Press: New York, 1995) Ch.2 .
3. Liboff, R. L. *Introductory Quantum Mechanics* (Addison-Wesley, Reading, MA, 1980) p. 77.
4. Sakurai, J. J. *Modern Quantum Mechanics, Revised Edition* (Addison-Wesley, Reading, MA, 1994).

1.3. APPENDIX: PROPERTIES OF OPERATORS

- 1) The inverse of \hat{A} (written \hat{A}^{-1}) is defined by

$$\hat{A}^{-1}\hat{A} = \hat{A}\hat{A}^{-1} = \hat{\mathbf{I}} \quad (1.50)$$

- 2) The transpose of \hat{A} (written A^T) is

$$\left(A^T\right)_{nq} = A_{qn} \quad (1.51)$$

If $A^T = -A$ then the matrix is antisymmetric

- 3) The trace of \hat{A} is defined as

$$Tr(\hat{A}) = \sum_q A_{qq} \quad (1.52)$$

- 4) The Hermetian Adjoint of \hat{A} (written \hat{A}^\dagger) is

$$\begin{aligned} \hat{A}^\dagger &= \left(\hat{A}^T\right)^* \\ \left(\hat{A}^\dagger\right)_{nq} &= \left(\hat{A}_{qn}\right)^* \end{aligned} \quad (1.53)$$

- 5) \hat{A} is Hermetian if

$$\begin{aligned} \hat{A}^\dagger &= \hat{A} \\ \left(\hat{A}^T\right)^* &= A \end{aligned} \quad (1.54)$$

If \hat{A} is Hermetian, then \hat{A}^n is Hermetian and $e^{\hat{A}}$ is Hermetian.

- 6) \hat{A} is a unitary operator if:

$$\begin{aligned} \hat{A}^\dagger &= \hat{A}^{-1} \\ \left(\hat{A}^T\right)^* &= \hat{A}^{-1} \\ \hat{A}\hat{A}^\dagger = 1 &\Rightarrow \left(\hat{A}\hat{A}^\dagger\right)_{nq} = \delta_{nq} \end{aligned} \quad (1.55)$$