

Physics 221B Lecture Notes

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1 Symmetries and Angular Momentum

Sakurai Chapters 3 and 4

1.1 Symmetries

Sakurai 4.1, 4.2, 4.4

If a change in reference frame does not change the expected outcome, then that change is called a symmetry of the system. Systems may either be continuous or discrete, for example translational symmetry in a vacuum versus in a lattice. There are two views of symmetries:

1. change the basis vectors
2. change the state

Mathematically, we represent this in terms of a symmetry transformation S , where:

$$|\psi'\rangle = S|\psi\rangle \quad (1.1)$$

Since there is no change in the expected outcome, the overlaps are preserved:

$$|\langle\psi|\phi\rangle|^2 = |\langle S\psi|S\phi\rangle|^2 \quad (1.2)$$

Wigner's Theorem states that every symmetry transformation corresponds to either

1. a linear, unitary operator

$$S(a|a\rangle + b|b\rangle) = aS|a\rangle + bS|b\rangle, \quad \langle Sa|Sb\rangle = \langle a|b\rangle \quad (1.3)$$

2. or, an anti-linear, anti-unitary operator¹

$$S(a|a\rangle + b|b\rangle) = a^*S|a\rangle + b^*S|b\rangle, \quad \langle Sa|Sb\rangle = (\langle a|b\rangle)^* \quad (1.4)$$

The matrix elements of an operator A transform under symmetry transformation² as:

$$\langle\phi|A|\psi\rangle \mapsto \langle\phi|S^\dagger AS|\psi\rangle \quad (1.5)$$

Where the adjoint A^\dagger of an operator A is:

$$\text{linear: } \langle a|A^\dagger|b\rangle = (\langle b|A|a\rangle)^* \quad (1.6)$$

$$\text{anti-linear: } \langle a|A^\dagger|b\rangle = \langle b|A|a\rangle \quad (1.7)$$

Now, suppose that a unitary operator U corresponds to a continuous symmetry, and ϵ is a small parameter. Then we say that the hermitian operator A is the generator of the transformation if:

$$U(\epsilon) = e^{i\epsilon A} \quad (1.8)$$

As an alternative to defining symmetries by the conservation of overlaps, we may consider the Schrödinger equation:

$$H|\psi\rangle = i\hbar \frac{\partial}{\partial t} |\psi\rangle \quad (1.9)$$

¹Such as the complex conjugation operator K .

²Also known as a similarity transformation.

Which becomes under a time-independent symmetry transformation U :

$$(UHU^{-1})U|\psi\rangle = \pm i\hbar \frac{\partial}{\partial t} U|\psi\rangle \quad (1.10)$$

Where $+$ corresponds to unitary U and $-$ corresponds to anti-unitary U . Now, if $UHU^{-1} = \pm H$, and U is unitary, then $U|\psi\rangle$ satisfies the same form of the Schrödinger equation, and we say that the system has the symmetry corresponding to U .

1.1.1 Parity

Parity is the symmetry corresponding to reversal of all spatial coordinates (ex. taking a right handed coordinate system and turning it into a left handed coordinate system):

$$|x'\rangle = |-x\rangle \quad (1.11)$$

We introduce the symmetry operator π , and see that:

$$\pi|x\rangle = |-x\rangle \quad (1.12)$$

$$\pi^2|x\rangle = |x\rangle \quad (1.13)$$

Since $\{|x\rangle\}$ is complete, we have that $\pi^2 = \mathbb{1}$, and so $\pi = \pi^{-1}$. Thence its eigenvalues are ± 1 .

In operator form, we have the transformations of x and p :

$$\pi x \pi^{-1} = -x \quad (1.14)$$

$$\pi p \pi^{-1} = -p \quad (1.15)$$

So if we apply this to angular momentum:

$$\pi L \pi^{-1} = (\pi x \pi^{-1}) \times (\pi p \pi^{-1}) \quad (1.16)$$

$$= (-1)^2 x \times p \quad (1.17)$$

$$= L \quad (1.18)$$

Now, parity gives us the simplest example of a selection rule. Suppose that:

$$\pi|\phi_a\rangle = (-1)^a|\phi_a\rangle \quad a = 0, 1 \quad (1.19)$$

$$\pi|\phi_b\rangle = (-1)^b|\phi_b\rangle \quad b = 0, 1 \quad (1.20)$$

$$\pi A_c \pi^{-1} = (-1)^c A_c \quad c = 0, 1 \quad (1.21)$$

Then we can write:

$$\langle\phi_b|A_c|\phi_a\rangle = \langle\phi_b|\pi^{-1}\pi A_c \pi^{-1}\pi|\phi_a\rangle \quad (1.22)$$

$$= (-1)^{a+b+c}\langle\phi_b|A_c|\phi_a\rangle \quad (1.23)$$

And evidently, if $a + b + c$ is odd, then:

$$\langle\phi_b|A_c|\phi_a\rangle = -\langle\phi_b|A_c|\phi_a\rangle \quad (1.24)$$

So $\langle\phi_b|A_c|\phi_a\rangle = 0$, which is a selection rule that rules out many matrix elements.

1.1.2 Time Reversal Symmetry

An symmetry transformation corresponding to an anti-unitary operator is time reversal symmetry. We have the familiar relation:

$$|\psi(t)\rangle = U(t, 0)|\psi(0)\rangle \quad (1.25)$$

$$= e^{-iHt}|\psi(0)\rangle \quad (1.26)$$

Now, we introduce the time reversal operator Θ , where:

$$\Theta|\psi(t)\rangle = e^{iHt}\Theta|\psi(0)\rangle \quad (1.27)$$

So we have the relation $\Theta e^{-iHt} = e^{iHt}\Theta$, from which we may show by illustrative example³ or by the Schrödinger equation that Θ is anti-linear and anti-unitary, and that if a system is time-reversal invariant:

$$[\Theta, H] = 0 \quad (1.28)$$

In such a system, if we have an eigenstate $|n\rangle$, we have:

$$H|n\rangle = E_n|n\rangle \quad (1.29)$$

$$H\Theta|n\rangle = E_n\Theta|n\rangle \quad (1.30)$$

So we see that $|n\rangle$ and $\Theta|n\rangle$ are either the same state or there is a Kramer's degeneracy.

The time-reversal operator acts as:

$$\Theta p \Theta^{-1} = -p \quad (1.31)$$

$$\Theta L \Theta^{-1} = -L \quad (1.32)$$

$$\Theta S \Theta^{-1} = -S \quad (1.33)$$

In fact Θ acts for complex conjugation operator K on spin as⁴:

$$\Theta = e^{-i\pi S_y/\hbar} K \quad (1.34)$$

So we see that for spins $\Theta^2 = (-1)^{2j}$, and so:

$$\Theta^2|j, m\rangle = \begin{cases} +|j, m\rangle & j = 0, 1, 2, \dots \\ -|j, m\rangle & j = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots \end{cases} \quad (1.35)$$

1.2 Angular Momentum

Sakurai 3.1, 3.2, 3.5, 3.8, 3.11

The total angular momentum $J = L + S$ is a generator as in Eq. 1.8. In fact, J is the generator corresponding to the symmetry transformation of rotations about the axis specified by \hat{n} :

$$U(R(\omega, \hat{n})) = \exp\left[-\frac{i\omega}{\hbar}(J \cdot \hat{n})\right] \quad (1.36)$$

$$\approx \mathbb{1} - \frac{i\omega}{\hbar}(J \cdot \hat{n}) + O(\omega^2) \quad (1.37)$$

We define the overlap to be:

$$D_{m', m}^j = \langle j, m' | U(R) | j, m \rangle \quad (1.38)$$

³Ex. the free particle, $H_0 = p^2/2m$.

⁴Theorem: every anti-unitary operator V can be written as $V = KU$, or $V = UK$ for some unitary U and the complex conjugation operator K .

1.2.1 Review of Angular Momentum

We have the relations for angular momentum:

$$L = x \times p \quad (1.39)$$

$$[L_i, L_j] = i\hbar \sum_k \epsilon_{ijk} L_k \quad (1.40)$$

These algebraic relations define a Lie algebra. We now recall the raising and lowering operators:

$$J_{\pm} = J_x \pm iJ_y \quad (1.41)$$

Where we have the relation for $j = n/2$ for $n \in \mathbb{N}$ and $m \in \{-j, -j+1, \dots, j\}$:

$$J_{\pm}|j, m\rangle = \sqrt{(j \mp m)(j \pm m + 1)} \hbar |j, m \pm 1\rangle \quad (1.42)$$

Additionally, we note the eigenvalue relations:

$$J^2|j, m\rangle = j(j+1) \hbar^2 |j, m\rangle \quad (1.43)$$

$$J_z|j, m\rangle = m\hbar |j, m\rangle \quad (1.44)$$

1.2.2 Tensor Operators

Using the mathematics of tensor operators, we may systematically approach problems involving angular momentum. First, we define the Cartesian tensor operator:

$$T_{ijk} = \sum_{i', j', k'} R_{ii'} R_{jj'} R_{kk'} \quad (1.45)$$

Now we introduce the spherical rank- k tensor T_q^k which has $2k+1$ components. Spherical tensors transform as:

$$U^\dagger(R) T_q^k U(R) = \sum_{q'=-k}^k (D_{q,q'}^k)^* T_{q'}^k \quad (1.46)$$

If we take the infinitesimal rotations and make them finite, we arrive at the following commutation rules:⁵

$$[J \cdot \hat{n}, T_q^k] = \sum_{q'} T_{q'}^k \langle k, q' | J \cdot \hat{n} | k, q \rangle \quad (1.47)$$

$$[J_z, T_q^k] = \hbar q T_q^k \quad (1.48)$$

$$[J_{\pm}, T_q^k] = \hbar \sqrt{(k \mp q)(k \pm q + 1)} T_{q \pm 1}^k \quad (1.49)$$

1.2.3 Addition of Angular Momentum

Suppose we have two mutually observable angular momenta represented by the total angular momentum operators J_1 and J_2 :

$$[J_{1,i}, J_{2,j}] = 0 \quad (1.50)$$

Which means we have the parallel to Eq. 1.43:

$$J_{1|2}^2 |j_1, j_2; m_1, m_2\rangle = j_{1|2}(j_{1|2} + 1) \hbar^2 |j_1, j_2; m_1, m_2\rangle \quad (1.51)$$

$$J_{1|2}^z |j_1, j_2; m_1, m_2\rangle = m_{1|2} \hbar |j_1, j_2; m_1, m_2\rangle \quad (1.52)$$

Which also hold for $J_{1|2} \mapsto J$ where:

$$J = J_1 + J_2 \quad (1.53)$$

⁵Alternately, these commutation relations fully characterize spherical tensor operators.

1.2.4 Wigner-Eckart Theorem

We saw with parity that there can be selection rules which enable us to say that many matrix elements of an operator are zero. A powerful selection rule comes in the form of the Wigner-Eckart Theorem. One consequence is the m -selection rule:

$$\langle \alpha'; j', m' | T_q^k | \alpha; j, m \rangle = 0, \quad \text{unless } |m' - m| = q \quad (1.54)$$

This selection rule may be used if we note that z acts as a rank-1 spherical tensor, so in the Hydrogen atom:

$$\langle n' \ell' m' | z | n \ell m \rangle = 0, \quad \text{unless } |m' - m| = 0 \quad (1.55)$$

We also have:

$$\langle n' \ell' m' | z | n \ell m \rangle = 0, \quad \text{unless } |\ell' - \ell| = 1 \quad (1.56)$$

Now we introduce the inverse Clebsch-Gordon coefficient $C_{q,m}^{j,m}$ where for some rank- k spherical tensor T_q^k we have:⁶

$$T_q^k | \alpha; j, m \rangle = C_{q,m}^{j,m} | k; j, m \rangle \quad (1.57)$$

It may then be shown that for a constant independent of m , m' , and q that:

$$\langle \alpha'; j', m' | T_q^k | \alpha; j, m \rangle = \text{constant} \langle jk; mq | k; j' m' \rangle \quad (1.58)$$

This is the Wigner-Eckart Theorem where the constant is given by:

$$\text{constant} = \frac{\langle \alpha'; j' || T^k || \alpha; j \rangle}{\sqrt{2j+1}} \quad (1.59)$$

Now we note that unless $j = j'$ and $m = m'$:

$$\langle \alpha'; j' m' | \alpha; j, m \rangle = 0 \quad (1.60)$$

This gives us selection rule for the matrix elements of T_q^k .

In the example of the z -component of angular momentum:

$$\langle \alpha'; j' m' | J_z | \alpha; j, m \rangle = m \langle \alpha'; j' m' | \alpha; j, m \rangle \quad (1.61)$$

When $j = j'$ and T_q^k is a vector operator V , the Wigner-Eckart Theorem simplifies and we have the Projection Theorem wherein:

$$\langle \alpha'; j', m' | V_q | \alpha; j, m \rangle = \frac{\langle \alpha'; j', m' | J \cdot V | \alpha; j, m \rangle}{\hbar^2 j(j+1)} \langle j, m' | J_q | j, m \rangle \quad (1.62)$$

⁶Clebsch-Gordon coefficients are tedious, but Mathematica and WolframAlpha are there to help with the command `ClebschGordan[j1, m1, j2, m2, j, m]`

2 Perturbation Theory

Sakurai Chapter 5

Only a few problems are exactly solvable, in that we have analytic expressions for their eigenfunctions $|\psi_n^{(0)}\rangle$ and eigenvalues $E_n^{(0)}$:

$$H_0|\psi_n^{(0)}\rangle = E_n^{(0)}|\psi_n^{(0)}\rangle \quad (2.1)$$

Yet, the behavior we are interested in is often that of a slightly “perturbed” system. Namely, we can consider perturbations H' of strength λ around the solutions of a problem with a known solution H_0 :

$$H = H_0 + \lambda H' \quad (2.2)$$

As an example, we may consider an electron in a system of two quantum dots with onsite potentials V_L and V_R , and unperturbed eigenstates $|L\rangle = (1, 0)^T$ and $|R\rangle = (0, 1)^T$ and then add a perturbation to represent tunneling between the left and right dots:

$$H = \begin{pmatrix} V_L & 0 \\ 0 & V_R \end{pmatrix} + \begin{pmatrix} 0 & \lambda \\ \lambda & 0 \end{pmatrix} \quad (2.3)$$

While this perturbed two state system has an exact solution, in many situations we will not be so lucky, so we look for a solution of the form^{7 8}:

$$|\psi_n\rangle = |\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + \dots \quad (2.4)$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \quad (2.5)$$

Where we have:

$$(H_0 + \lambda H')|\psi_n\rangle = E_n|\psi_n\rangle \quad (2.6)$$

2.1 Time Independent Non-Degenerate Perturbation Theory

Sakurai 5.1

Rearranging Eq. 2.6, we find that:

$$\lambda H' \left(|\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \dots \right) = \left(E_n^{(0)} + \lambda E_n^{(1)} + \dots \right) \left(|\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \dots \right) - H_0 \left(|\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \dots \right) \quad (2.7)$$

Equating powers of λ in Eq. 2.7 to order λ^0 , we regain the time-independent Schrödinger equation for the unperturbed system:

$$0 = E_n^{(0)}|\psi_n^{(0)}\rangle - H_0|\psi_n^{(0)}\rangle \quad (2.8)$$

Equating powers of λ in Eq. 2.7 to order λ^1 :

$$\lambda H'|\psi_n^{(0)}\rangle = E_n^{(0)}\lambda|\psi_n^{(1)}\rangle + \lambda E_n^{(1)}|\psi_n^{(0)}\rangle - H_0\lambda|\psi_n^{(1)}\rangle \quad (2.9)$$

Applying $\langle\psi_n^{(0)}|$ to Eq. 2.9, we find the first-order corrections to the energies:

$$\lambda E_n^{(1)} = \langle\psi_n^{(0)}|\lambda H'|\psi_n^{(0)}\rangle \quad (2.10)$$

⁷Theorem: for finite dimensional Hilbert spaces, there is always a finite radius of convergence. For infinite dimensional spaces, the radius of convergence is often 0, but the first few terms may still be useful.

⁸The overlap $\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle$, can take any value and be consistent with the equations in this section, so we take $\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle = 0$.

If instead we apply $\langle \psi_m^{(0)} |$ to Eq. 2.9, where $\langle \psi_m^{(0)} | \psi_n^{(0)} \rangle = \delta_{mn}$, and we assume the energies are non-degenerate ($|E_m^{(0)} - E_n^{(0)}| \neq 0$) we find the first-order corrections to the wavefunctions:

$$\lambda \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle = \frac{\langle \psi_m^{(0)} | \lambda H' | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \quad m \neq n \quad (2.11)$$

Equating powers of λ in Eq. 2.7 to order λ^2 :

$$\lambda H' \lambda | \psi_n^{(1)} \rangle = E_n^{(0)} \lambda^2 | \psi_n^{(2)} \rangle + \lambda E_n^{(1)} \lambda | \psi_n^{(1)} \rangle + \lambda^2 E_n^{(2)} | \psi_n^{(0)} \rangle - H_0 \lambda^2 | \psi_n^{(2)} \rangle \quad (2.12)$$

Applying $\langle \psi_n^{(0)} |$ to Eq. 2.12, inserting the identity as $\mathbb{1} = \sum_m | \psi_m^{(0)} \rangle \langle \psi_m^{(0)} |$, and through algebraic manipulations, we find the second-order corrections to the energies:

$$\lambda^2 E_n^{(2)} = \sum_{m \neq n} \frac{|\langle \psi_m^{(0)} | \lambda H' | \psi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}} \quad (2.13)$$

Likewise, applying $\langle \psi_m^{(0)} |$ to Eq. 2.12, we find the second-order corrections to the wavefunctions:

$$\lambda^2 \langle \psi_m^{(0)} | \psi_n^{(2)} \rangle = \sum_{k \neq n} \frac{\langle \psi_m^{(0)} | \lambda H' | \psi_k^{(0)} \rangle \langle \psi_k^{(0)} | \lambda H' | \psi_n^{(0)} \rangle}{(E_n^{(0)} - E_m^{(0)})(E_n^{(0)} - E_k^{(0)})} - \frac{\langle \psi_n^{(0)} | \lambda H' | \psi_n^{(0)} \rangle \langle \psi_m^{(0)} | \lambda H' | \psi_n^{(0)} \rangle}{(E_n^{(0)} - E_m^{(0)})^2} \quad (2.14)$$

We note that for each of the equations for the corrections to the wave functions above we may use:

$$\lambda^N | \psi_n^{(N)} \rangle = \sum_m \lambda^N | \psi_m^{(0)} \rangle \langle \psi_m^{(0)} | \psi_n^{(N)} \rangle = \sum_m \lambda^N \langle \psi_m^{(0)} | \psi_n^{(N)} \rangle | \psi_m^{(0)} \rangle \quad (2.15)$$

2.2 Time Independent Degenerate Perturbation Theory

Sakurai 5.2

The relations for degenerate perturbation theory follow identically as those of non-degenerate perturbation theory do, except that now we require that the perturbation be diagonal in the degenerate subspace. To see this, we note that once we arrive at the expression of Eq. 2.11, if $E_n^{(0)} = E_m^{(0)}$, the expression only makes sense if $\langle \psi_m^{(0)} | \lambda H' | \psi_n^{(0)} \rangle = 0$:

$$E_n^{(0)} \lambda \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle - E_m^{(0)} \lambda \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle = \langle \psi_m^{(0)} | \lambda H' | \psi_n^{(0)} \rangle \quad (2.16)$$

Hence, we choose the unperturbed basis of the degenerate subspace, $\{ | \psi_n^{(0)} \rangle \}$, such that $\lambda H'$ is diagonal. To find these states, choose any set linearly independent states $\{ | \phi_n^{(0)} \rangle \}$ that span the degenerate subspace, then solve the secular equation, where $\lambda V_{ij} = \langle \phi_i^{(0)} | \lambda H' | \phi_j^{(0)} \rangle$, and $E_n^{(1)}$ are the first order energy shifts:

$$\begin{pmatrix} \lambda V_{11} & \lambda V_{12} & \dots \\ \lambda V_{21} & \lambda V_{22} & \dots \\ \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} \langle \phi_1^{(0)} | \psi_n^{(0)} \rangle \\ \langle \phi_2^{(0)} | \psi_n^{(0)} \rangle \\ \vdots \end{pmatrix} = \lambda E_n^{(1)} \begin{pmatrix} \langle \phi_1^{(0)} | \psi_n^{(0)} \rangle \\ \langle \phi_2^{(0)} | \psi_n^{(0)} \rangle \\ \vdots \end{pmatrix} \quad (2.17)$$

To arrive at the secular equation, we introduce the projection operator onto the degenerate subspace $P^{(0)}$ spanned by $\{ | \phi_n^{(0)} \rangle \}$, and introduce the projection operator onto the remaining states $P_{\perp}^{(0)} = \mathbb{1} - P^{(0)}$. Since we are interested in stationary states, we may consider the time-independent Schrödinger Equation:

$$H | \psi_n^{(0)} \rangle = E | \psi_n^{(0)} \rangle \quad (2.18)$$

Collecting terms of order λ and applying $P^{(0)}$ on the left and the right:

$$(P^{(0)}\lambda H'P^{(0)} - \lambda E_n^{(1)})|\psi_n^{(0)}\rangle = 0 \quad (2.19)$$

Which is precisely Eq. 2.17, where the eigenstates of $P^{(0)}\lambda H'P^{(0)}$ are the correct zero-order states, and the corresponding eigenvalues are the first-order energy corrections.

For higher order corrections to the states and the energies, we may use the corresponding formulas for non-degenerate perturbation theory, except in the summations, where we exclude all contributions from $\{|\psi_n^{(0)}\rangle\}$.⁹

2.3 Applications of Time Independent Perturbation Theory to Hydrogenic Atoms

Mostly Sakurai 5.3

Hydrogen, ionized Helium, and doubly ionized Lithium have one electron outside attracted to a nucleus, while hydrogenic atoms such as Sodium, Potassium, have one electron outside a closed shell surrounding a nucleus. For Hydrogen, where the Coulomb potential is unshielded, the unperturbed Hamiltonian is:

$$H_0 = \frac{p^2}{2m} - \frac{Ze^2}{r} \quad (2.20)$$

The energies of the hydrogen atom given by the principle quantum number n , where $k = 1/4\pi\epsilon_0$:

$$E_n^{(0)} = -\frac{1}{n^2} \frac{mk^2 Z^2 e^4}{2\hbar^2} \quad (2.21)$$

The Hydrogen wavefunctions expressed in the position basis are separable into a radial wavefunction $R_{n\ell}(r)$ and a spherical harmonic $Y_\ell^m(\theta, \varphi)$ as:

$$|n\ell m\rangle = R_{n\ell}(r)Y_\ell^m(\theta, \varphi) \quad (2.22)$$

2.3.1 Stark Effect

Sakurai 5.1 and 5.2

Here we consider a Hydrogen atom in an applied electric field $\mathcal{E}\hat{z}$, which perturbs the Hamiltonian as:

$$H' = -e\mathcal{E}z \quad (2.23)$$

For the non-degenerate case,¹⁰ we consider the ground state of Hydrogen, $|100\rangle$.

The first order energy correction is zero by the Wigner-Eckart Theorem,¹¹ Eq. 1.58, since $|\ell' - \ell| \neq 1$:

$$E_1^{(1)} = -e\mathcal{E}\langle 100|z|100\rangle = 0 \quad (2.24)$$

However, second order energy correction is non-vanishing:

$$E_1^{(2)} = -e^2\mathcal{E}^2 \sum_{n'=2}^{\infty} \frac{|\langle 100|z|n'10\rangle|^2}{E_{n'}^{(0)} - E_n^{(0)}} = -\frac{9a_0^3}{4}\mathcal{E}^2 \quad (2.25)$$

We note that this corresponds to an induced dipole moment d of:

$$d = -\frac{\partial E}{\partial \mathcal{E}} = \frac{9a_0^3}{2}\mathcal{E} \quad (2.26)$$

For the degenerate case,¹² we consider the first excited states of Hydrogen: $|200\rangle$, $|21-1\rangle$, $|210\rangle$, and $|211\rangle$.

⁹If degeneracy is not lifted by the first-order energy shifts, then $\{|\psi_n^{(0)}\rangle\}$ are the eigenstates of the secular equation $(P^{(0)}\lambda H'P^{(0)} - \lambda E_n^{(1)})|\psi_n^{(0)}\rangle = 0$.

¹⁰Neither H_0 nor H' have spin dependent terms, so the spin degrees of freedom may be neglected here.

¹¹ $|n\ell m\rangle$ has parity $(-1)^\ell$, while z has parity -1 , so with $\ell = 0$, we are integrating an odd function over all space.

¹²As in the non-degenerate case, we can ignore spin.

By the Wigner-Eckart Theorem, $\langle n\ell m|z|n'\ell'm'\rangle$ vanish unless $|\ell' - \ell| = 1$ and $|m' - m| = 0$, so the only non-vanishing terms are now $\langle 200|z|210\rangle = (\langle 210|z|200\rangle)^*$. So, we evaluate with $z = r \cos(\theta)$:

$$\langle 200|z|210\rangle = \int_0^\infty r^2 dr \int_0^\pi \sin(\theta) d\theta \int_0^{2\pi} d\varphi [R_{20}(r)Y_0^0(\theta, \varphi)]^* r \cos(\theta) [R_{21}(r)Y_1^0(\theta, \varphi)] = 3a_0 \quad (2.27)$$

In matrix form the perturbation is:

$$H' = -3a_0 e\mathcal{E} \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \quad (2.28)$$

Which may be diagonalized. Doing so, we find that the $|21 \pm 1\rangle$ states are unperturbed, while the other two states are $(|210\rangle \pm |200\rangle)/\sqrt{2}$, with energies $E_2^{(0)} \mp 3a_0 e\mathcal{E}$.

We note that the states perturbed states have permanent dipole moments of:

$$d_\pm = -\frac{\partial E_\mp}{\partial \mathcal{E}} = \mp 3a_0 e \quad (2.29)$$

2.3.2 Zeeman Effect

Sakurai 5.3

In this section only, we write electron mass m_e and magnetic quantum number m to avoid ambiguity.

Here we consider a Hydrogen atom in an applied magnetic field $B\hat{z}$, in which the momentum is the canonical momentum $p \rightarrow p - eA/c$, so with the vector potential taken as $A = B(-y\hat{x} + x\hat{y})/2$, we have:

$$H = \frac{1}{2m_e} \left(p - \frac{e}{c}A \right)^2 - \frac{Ze^2}{r} \quad (2.30)$$

With this vector potential, for $L_z = xp_y - yp_x$, and dropping the $(eB/2c)^2(x^2 + y^2)/2m_e$ term, we have:

$$H = H_0 - \frac{eB}{2m_e c} L_z \quad (2.31)$$

Generalizing this to include spin (with a g -factor of roughly 2), we have a perturbation:

$$H'_B = -\frac{eB}{2m_e c} (L_z + gS_z) \approx -\frac{eB}{2m_e c} (J_z + S_z) \quad (2.32)$$

Evaluating the expectation values $\langle J_z \rangle$ and $\langle S_z \rangle$, one finds that for:

$$\Delta E_B = -\frac{eB}{2m_e c} \left(m\hbar \pm \frac{m\hbar}{2\ell + 1} \right) \quad (2.33)$$

2.3.3 Spin-Orbit Interaction

Sakurai 5.3

Since the electron is moving and there is an electric field, the electron experiences a magnetic field of $B_\perp \approx -v \times E/c$ where the electric field is $E = -(1/e)\nabla V$. So with $V = -Ze^2/r$ and $L = x \times p$, we suspect

a spin-orbit potential:

$$H'_{SO} = -\frac{eg}{2mc} S \cdot -\frac{v}{c} \times E \quad (2.34)$$

$$= \frac{eg}{2mc} S \cdot \left[\frac{p}{mc} \times \frac{x}{r} \frac{1}{e} \frac{d}{dr} \frac{Ze^2}{r} \right] \quad (2.35)$$

$$= \frac{gZe^2}{2m^2c^2} \frac{L \cdot S}{r^3} \quad (2.36)$$

This is nearly correct, but due to Thomas precession, $g \rightarrow g - 1$:

$$H'_{SO} = \frac{(g-1)Ze^2}{2m^2c^2} \frac{L \cdot S}{r^3} \quad (2.37)$$

We recall the Landé Interval Rule:

$$\langle L \cdot S \rangle = \frac{\hbar^2}{2} \begin{cases} \ell & j = \ell + \frac{1}{2} \\ -(\ell + 1) & j = \ell - \frac{1}{2} \end{cases} \quad (2.38)$$

It can be shown that:

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{n^3 a_0^3} \frac{1}{\ell(\ell + \frac{1}{2})(\ell + 1)} \quad (2.39)$$

So we find:

$$\Delta E_{SO} = \frac{(g-1)Ze^2\hbar^2}{4m^2c^2n^3a_0^3} \frac{1}{\ell(\ell + \frac{1}{2})(\ell + 1)} \begin{cases} \ell & j = \ell + \frac{1}{2} \\ -(\ell + 1) & j = \ell - \frac{1}{2} \end{cases} \quad (2.40)$$

2.3.4 Spin-Orbit versus Zeeman

In a weak magnetic field, $H'_B \ll H'_{SO}$, there is spherical symmetry, so the operators J^2 , L^2 , S^2 , and J_z are valid. Additionally, they form a complete set of commuting observables for our problem and they commute with $L \cdot S$ as we note that for $J = L + S$:

$$L \cdot S = \frac{1}{2} [J^2 - L^2 - S^2] \quad (2.41)$$

In a strong magnetic field, $H'_{SO} \ll H'_B$, spherical symmetry is broken and so J^2 and $L \cdot S$ are no longer good quantum numbers (but J_z is). However, L^2 , S^2 , L_z , and S_z form a complete set of commuting observables for our problem and they commute with $L_z + gS_z$, so we may proceed with this CSCO.

We summarize in the following table:

| Spin-Orbit or Zeeman? | |
|-----------------------|-----------|
| | Dominant |
| Small B | H'_{SO} |
| Large B | H'_B |

2.4 Time Dependent Perturbation Theory

Sakurai 5.5, 5.7, 5.8

Here we consider Hamiltonians of the form:

$$H = H_0 + H'(t) \quad (2.42)$$

With a time-dependent perturbation, there is no longer any particular Hamiltonian to diagonalize, so instead we try to find the time evolution unitary $U(t)$:

$$|\psi(t)\rangle = U(t)|\psi(0)\rangle \quad (2.43)$$

Now, the eigenfunctions $|n\rangle$ and energy eigenvalues E_n of H_0 are known, and we recall that if $|\psi(0)\rangle = \sum_n c_n |n\rangle$, and $H'(t) = 0$, then:

$$|\psi(t)\rangle = \sum_n c_n e^{-iE_n t/\hbar} |n\rangle \quad (2.44)$$

With $U_0(t) = e^{-iH_0 t/\hbar}$, this is precisely the expression:

$$|\psi(t)\rangle = U_0(t)|\psi(0)\rangle \quad (2.45)$$

This suggests that we can write $U(t) = U_0(t)U'(t)$. Recalling that the Schrödinger Equation also holds for the time evolution operator, we have:

$$i\hbar \frac{\partial U(t)}{\partial t} = H(t)U(t) \quad (2.46)$$

Evaluating $\partial_t U(t)$ using the product rule and rearranging, we find:

$$i\hbar \frac{\partial U'(t)}{\partial t} = V_I(t)U'(t) \quad (2.47)$$

Where we have defined:

$$V_I(t) \equiv U_0^\dagger(t)V(t)U_0(t) \quad (2.48)$$

This brings us to the Interaction Picture of Quantum Mechanics, wherein states and operators are transformed from the Schrödinger Picture:

$$|\psi(t)\rangle_I = U_0^\dagger(t)|\psi(t)\rangle_S \quad (2.49)$$

$$A_I(t) = U_0^\dagger(t)A_S U_0(t) \quad (2.50)$$

We see that the interaction picture is akin to the Heisenberg picture with $H \rightarrow H_0$.

2.4.1 Dyson Series

Now if we want to solve Eq. 2.47, we can apply $\langle n|$ from the left and sum over a resolution of the identity, with $V_{ij} = \langle i|H'(t)|j\rangle$ and $\omega_{ij} = (E_i - E_j)/\hbar$, and write in matrix form. This is rarely exactly solvable:

$$i\hbar \begin{pmatrix} \dot{c}_1 \\ \dot{c}_2 \\ \vdots \end{pmatrix} = \begin{pmatrix} V_{11} & V_{12}e^{i\omega_{12}t} & \dots \\ V_{21}e^{i\omega_{21}t} & V_{22} & \dots \\ \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix} \quad (2.51)$$

Alternatively, we may consider a modification to Eq. 2.47, where $U_I(t, t_0) = U'(t)U'(t_0)^{-1}$, so we have:

$$i\hbar \frac{\partial U_I(t)}{\partial t} = V_I(t)U_I(t) \quad (2.52)$$

Or as an integral equation, noting $U_I(t_0, t_0) = \mathbb{1}$:

$$U_I(t, t_0) = \mathbb{1} - \frac{i}{\hbar} \int_{t_0}^t dt' V_I(t')U_I(t', t_0) \quad (2.53)$$

Which suggests an iterative solution. To second order¹³:

$$U_I(t, t_0) = \mathbb{1} - \frac{i}{\hbar} \int_{t_0}^t dt' V_I(t') + \left(\frac{-i}{\hbar}\right)^2 \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' V_I(t')V_I(t'') \quad (2.54)$$

Generalizing to an infinite product, we have for the time-ordering operator \mathcal{T} :

$$U_I(t, t_0) = \mathcal{T} \exp\left(-\frac{i}{\hbar} \int_{t_0}^t dt' V_I(t')\right) \quad (2.55)$$

Now, since there is no Hamiltonian per se for whose eigenstates solve the time-dependent problem, we instead consider the transition probability between states $|a\rangle$ and $|b\rangle$ as a result of a time dependent perturbation given by U :

$$P_{a \rightarrow b}(t) = |\langle b|U(t)|a\rangle|^2 \quad (2.56)$$

We note that U_I captures the essential physics of the transition:

$$P_{a \rightarrow b}(t) = |\langle b|U_I(t)|a\rangle|^2 \quad (2.57)$$

If we evaluate this for an initial state $|a\rangle$ to a final state $|b\rangle$ using the iterative solution above, we obtain for $\omega_{ba} = (E_b - E_a)/\hbar$ and $V_{ba}(t) = \langle b|H'(t)|a\rangle$ the Dyson Series:

$$c_b^{(0)}(t) = \delta_{ba} \quad (2.58)$$

$$c_b^{(1)}(t) = -\frac{i}{\hbar} \int_{t_0}^t dt' e^{i\omega_{ba}t'} V_{ba}(t') \quad (2.59)$$

$$c_b^{(2)}(t) = -\frac{1}{\hbar^2} \sum_n \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' e^{i\omega_{bn}t'} V_{bn}(t') e^{i\omega_{na}t''} V_{na}(t'') \quad (2.60)$$

Note that the zeroth order term involves zero transitions ($a \rightarrow a$), the first order term involves one transition ($a \rightarrow b$), and the second order term involves two transitions ($a \rightarrow n \rightarrow b$). The transitions $a \rightarrow n$ and $n \rightarrow b$ are known as virtual transitions.

2.5 Constant Perturbation

Sakurai 5.7

Perhaps the simplest time dependence is a unit step function, $\theta(t)$, scaled to an amplitude V with the step at $t = 0$:¹⁴

$$H'(t) = \theta(t)V \quad (2.61)$$

¹³In general $[V_I(t_1), V_I(t_2)] \neq 0$, so the order of the operators matters.

¹⁴ V is an operator. It may be $V\mathbb{1}$ for a number V , or V may depend on other operators such as x , p , and s .

This perturbation is relevant for understanding nuclear decay and driven qubit systems.

Now, we use the first order of the Dyson Series in Eq. 2.59:

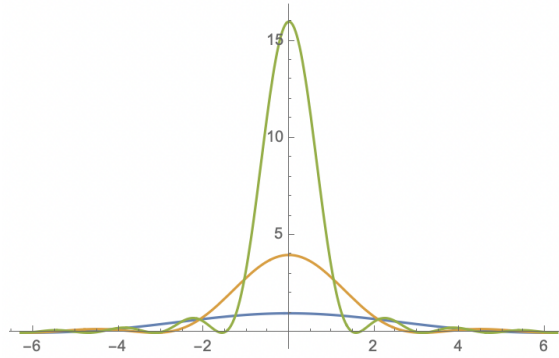
$$c_b^{(1)}(t) = -\frac{i}{\hbar} \int_{t_0}^t dt' e^{i\omega_{ba}t'} V_{ba}(t') = \frac{V_{ba}}{E_b - E_a} (1 - e^{i\omega_{ba}t}) \quad (2.62)$$

With algebra, we find:

$$|c_b^{(1)}(t)|^2 = \frac{4\hbar^2 |V_{ba}|^2}{\omega_{ni}^2} \sin^2(\omega_{ba}t/2) \quad (2.63)$$

2.5.1 Energy-Time Uncertainty Relation

Now, if we consider $|c_b^{(1)}(t)|^2(\omega)$, we see a function peaked at 0. We plot, where blue is $t = 0.5$, orange is $t = 1$, and green is $t = 2$:



The width of this peak depends on $\Delta t = t$ and on $\Delta E = \hbar\omega = |E_b - E_a|$, and in particular there is an Energy-Time Uncertainty Relation:

$$\Delta E \Delta t < 2\hbar \quad (2.64)$$

Near the time when the perturbation is turned on, the high frequency (high energy) components of the spectral decomposition of the potential are important, while at longer times, only low frequencies are important.

2.5.2 Fermi's Golden Rule

Considering the transition probability from a to b , with $E_a = E_b$, using Eq. 2.57 and Eq. 2.54, we find:

$$P_{a \rightarrow b}(t) = |\langle b | U_I(t) | a \rangle|^2 = \frac{|V_{ba}|^2}{\hbar^2} t^2 \quad (2.65)$$

This expression evidently breaks at large t , where $P > 1$. The solution to this problem is to consider a continuum of states rather than discrete states.

Let us consider $E_b \sim E_a$ and take the limit where states are closely spaced: $|E_n - E_{n+1}| \ll \hbar/t$. In this case, the probability of a transition from state a to one of the states with energy in the neighborhood of b is:

$$P_{a \rightarrow b} = 4|V_{ba}|^2 \int \frac{\sin^2(\omega_{ba}t/2)}{\hbar^2 \omega_{ba}^2} \rho(E) dE \xrightarrow{\lim t \rightarrow \infty} \text{proportional to } t \quad (2.66)$$

Now, if we consider the transition rate, and evaluate the integral, we find Fermi's Golden Rule:¹⁵

$$\frac{dP_{a \rightarrow b}}{dt} = \frac{2\pi}{\hbar} |V_{ba}|^2 \rho(E_b) \quad (2.67)$$

¹⁵Note that $\int_{-\infty}^{+\infty} dx \sin^2(x)/x^2 = \pi$.

If we evaluate to second order in the Dyson series, we find that Fermi's Golden rule becomes:

$$\frac{dP_{a \rightarrow b}}{dt} = \frac{2\pi}{\hbar} \left| V_{ba} + \sum_n \frac{V_{bn}V_{na}}{E_n - E_a} \right|^2 \rho(E_b) \quad (2.68)$$

If we assume that there is exactly one state at E_b , then we take $\rho(E_b) \mapsto \delta(E - E_b)$.

2.6 Harmonic Perturbation

Sakurai 5.7, 5.8

Another relevant time-dependent perturbation is the periodic perturbation:¹⁶

$$H'(t) = V e^{i\omega t} + V^\dagger e^{-i\omega t} \quad (2.69)$$

Evaluating the first order term of the Dyson Series, we find:

$$c_b^{(1)}(t) = \frac{1}{\hbar} \left[\frac{1 - e^{i(\omega_{ba} + \omega)t}}{\omega_{ba} + \omega} V_{ba} + \frac{1 - e^{i(\omega_{ba} - \omega)t}}{\omega_{ba} - \omega} V_{ba}^\dagger \right] \quad (2.70)$$

This expression is almost exactly the same as that for the constant perturbation in Eq. 2.62, so we note that at long times, $|c_b^{(1)}(t)|^2$ is only appreciable if $E_b \approx E_a \pm \hbar\omega$. The plus sign corresponds to absorption, while the minus sign corresponds to stimulated emission.

Fermi's Golden Rule 2.67 holds as above:

$$\frac{dP_{a \rightarrow b}}{dt} = \frac{2\pi}{\hbar} |V_{ba}|^2 \delta(E_b - (E_a - \hbar\omega)) + \frac{2\pi}{\hbar} |V_{ba}^\dagger|^2 \delta(E_b - (E_a + \hbar\omega)) \quad (2.71)$$

Noting that $|V_{ba}|^2 = |V_{ba}^\dagger|^2$, we arrive at the expression for detailed balancing:

$$\frac{\text{emission rate } a \rightarrow b}{\text{density of states at } b} = \frac{\text{absorption rate } b \rightarrow a}{\text{density of states at } a} \quad (2.72)$$

2.6.1 The Classical Radiation Field

For a monochromatic plane wave with direction of propagation \hat{n} and $k = |k|\hat{n}$ and linear polarization $\hat{\varepsilon}$, the vector potential is:

$$A(t) = A_0 \left[e^{i(k \cdot x - \omega t)} + e^{-i(k \cdot x - \omega t)} \right] \hat{\varepsilon} \quad (2.73)$$

From this, it can be shown that:¹⁷

$$H(t) = \frac{p^2}{2m} - \frac{e}{mc} A(t) \cdot p \quad (2.74)$$

Which is precisely a harmonic perturbation. Now, the transition rate is (for absorption):

$$\frac{dP_{a \rightarrow b}}{dt} = \frac{2\pi}{\hbar} \frac{e^2 A_0^2}{m^2 c^2} |\langle b | e^{ik \cdot x} \hat{\varepsilon} \cdot p | a \rangle|^2 \delta(E_b - (E_a + \hbar\omega)) \quad (2.75)$$

Noting that $\lambda_{\text{radiation}} = 2\pi/|k| \gg R_{\text{atom}} \sim Z/137$, we take the electric dipole approximation:

$$e^{ik \cdot x} = 1 + O(k \cdot x) \quad (2.76)$$

¹⁶ V is an operator. It may be $V\mathbb{1}$ for a number V , or V may depend on other operators such as x , p , and s .

¹⁷See Appendix A.

So if $x = \hat{x}$, we find

$$\langle b | e^{ik \cdot x} \hat{\varepsilon} \cdot p | a \rangle = \langle b | p_x | a \rangle \quad (2.77)$$

$$= \frac{m}{i\hbar} \langle b | [x, H_0] | a \rangle \quad (2.78)$$

$$= im\omega_{ba} \langle b | x | a \rangle \quad (2.79)$$

2.6.2 Absorption Cross Section of Classical Radiation

The absorption cross section is, with average energy density of $u = (|E|^2 + |B|^2)/16\pi$:

$$\sigma_{\text{abs}}(\omega) = \frac{\text{energy absorbed } (a \rightarrow b) \text{ by the atom per unit time}}{\text{energy flux of radiation field}} \quad (2.80)$$

$$= \frac{\hbar\omega(2\pi/\hbar) dP_{a \rightarrow b}}{\omega^2 A_0^2/c} \frac{dt}{dt} \quad (2.81)$$

$$= \frac{\hbar\omega(2\pi/\hbar)}{\omega^2 A_0^2/c} \frac{2\pi}{\hbar} \frac{e^2 A_0^2}{m^2 c^2} m^2 \omega_{ba}^2 |\langle b | x | a \rangle|^2 \delta(E_b - (E_a + \hbar\omega)) \quad (2.82)$$

$$= \frac{\omega_{ba}}{\omega} \frac{2\pi^2 e^2}{mc} f_{ba} \delta(\omega - \omega_{ba}) \quad (2.83)$$

Where we introduced the oscillator strength $f_{ba} = 2m\omega_{ba} |\langle b | x | a \rangle|^2 / \hbar$. It can be shown that:

$$\sum_b f_{ba} = 1 \quad (2.84)$$

So we have:

$$\int \sigma_{\text{abs}}(\omega) d\omega = \frac{2\pi^2 e^2}{mc} \quad (2.85)$$

We see that \hbar has disappeared, and this is indeed the same result as in classical electrodynamics.

3 Scattering

Sakurai Chapter 6

Scattering theory formulates a solution to the problem: if particles are initially far away from a potential, they can be treated as free plane waves, $|\phi_k\rangle$, but if they scatter off the potential, they will move in multiple directions. What directions do they move, and what does the potential look like (what is its cross section?)

3.1 Lippmann-Schwinger Equation

Sakurai 6.1, 6.2

One approach is to treat the potential as varying with time, for $\eta \rightarrow 0^+$, where $e^{-\infty} = 0$ and $e^0 = 1$:

$$H'(t) = Ve^{\eta t} \quad (3.1)$$

To solve this problem, we use a Greens function technique. First we note the Schrödinger equation can be written as:

$$\left(i\hbar \frac{\partial}{\partial t} - H_0\right) |\psi(t)\rangle = H'(t) |\psi(t)\rangle \quad (3.2)$$

Or with the Greens function $G(t, t_0)$:

$$\left(i\hbar \frac{\partial}{\partial t} - H_0\right) G(t, t_0) = \delta(t - t_0) \quad (3.3)$$

So the solution is for some wavevector k :

$$|\psi_k(t)\rangle = |\phi_k(t)\rangle + \int dt' G(t, t') H'(t') |\psi_k(t')\rangle \quad (3.4)$$

If we take $G(t, t_0)$ to be zero for $t < t_0$, we can write:

$$G(t, t_0) = -\frac{i}{\hbar} \theta(t - t') e^{-iH_0(t-t')/\hbar} \quad (3.5)$$

Inserting, we see:

$$|\psi_k(t)\rangle = |\phi_k(t)\rangle - \frac{i}{\hbar} \int_{-\infty}^t dt' e^{-iH_0 t/\hbar} e^{iH_0 t'/\hbar} V e^{\eta t'} |\psi_k(t')\rangle \quad (3.6)$$

Setting $t = 0$, and letting $|\psi_k(t)\rangle = e^{-iE_k t/\hbar} |\psi_k\rangle$ and $|\phi_k(t)\rangle = e^{-iE_k t/\hbar} |\phi_k\rangle$, we find:

$$|\psi_k\rangle = |\phi_k\rangle - \frac{i}{\hbar} \int_{-\infty}^0 dt' e^{iH_0 t'/\hbar} V e^{\eta t'} e^{-iE_k t'/\hbar} |\psi_k\rangle \quad (3.7)$$

Evaluating the integral and rearranging, we find the Lippmann-Schwinger equation for $\epsilon = \eta\hbar$:

$$|\psi_k\rangle = |\phi_k\rangle - \frac{V}{H_0 - E_k - i\epsilon} |\psi_k\rangle \quad (3.8)$$

There are actually two $|\psi_k\rangle$ states, $|\psi_k^{(+)}\rangle$ corresponding to the distant past, and $|\psi_k^{(-)}\rangle$ corresponding to the distant future. For these states, the Lippmann-Schwinger Equation is:

$$|\psi_k^{(\pm)}\rangle = |\phi_k\rangle \pm \frac{V}{E_k - H_0 \pm i\epsilon} |\psi_k^{(\pm)}\rangle \quad (3.9)$$

3.1.1 Scattering Amplitude and Differential Cross Section

Using complex line integrals, see Appendix B, it can be shown that:

$$G_{\pm}(r, r') = \left\langle r \left| \frac{\hbar^2/2m}{E_k - H_0 \pm i\epsilon} \right| r' \right\rangle = -\frac{1}{4\pi} \frac{e^{\pm k|r-r'|}}{|r-r'|} \quad (3.10)$$

It can then be shown, assuming that the potential is sufficiently localized to the origin that:

$$\langle r|\psi_k\rangle = \langle r|\phi_k\rangle - \frac{2m}{\hbar^2} \int d^3r' \frac{1}{4\pi} \frac{e^{ik|r-r'|}}{|r-r'|} V(r') \langle r'|\psi_k\rangle \quad (3.11)$$

Which means we can express the state as an incoming plane wave and an outgoing spherical wave:

$$\langle r|\psi_k\rangle = \frac{1}{(2\pi)^{3/2}} \left[e^{ik\cdot r} + \frac{e^{ikr}}{r} f(k, k') \right] \quad (3.12)$$

For a scattering amplitude defined as :

$$f(k, k') = -\frac{1}{4\pi} \frac{2m}{\hbar^2} (2\pi)^3 \int \frac{d^3r'}{(2\pi)^{3/2}} e^{-ik\cdot r'} V(r') \langle r'|\psi_k\rangle \quad (3.13)$$

$$= -\frac{1}{4\pi} \frac{2m}{\hbar^2} (2\pi)^3 \sum_{r'} \langle k'|r'\rangle \langle r'|V(r')|r'\rangle \langle r'|\psi_k\rangle \quad (3.14)$$

$$= -\frac{(2\pi)^3}{4\pi} \frac{2m}{\hbar^2} \langle k'|V(r)|\psi_k\rangle \quad (3.15)$$

The differential scattering cross section is:

$$\frac{d\sigma}{d\Omega} = \frac{\text{particles scattered into } d\Omega \text{ per unit time}}{\text{particles incident on unit area per unit time}} \quad (3.16)$$

Now, if we recall the probability current operator $J = (\hbar/m) \text{Im}(\langle \psi|\nabla|\psi\rangle)$, and for a probability flux through area $r^2 d\Omega$ is proportional to $|J|r^2 d\Omega$, we see:

$$\frac{d\sigma}{d\Omega} = |f(k, k')|^2 \quad (3.17)$$

3.2 Born Approximation

Sakurai 6.3

(Valid for high incident energies $V \ll \hbar^2 k^2/2m$)

In the first order Born approximation, the wavefunction is approximated as free:

$$\langle r|\psi_k\rangle \mapsto \langle r|\phi_k\rangle = \frac{e^{ik\cdot r}}{(2\pi)^{3/2}} \quad (3.18)$$

The scattering amplitude is then (to first order Born approximation):

$$f^{(1)}(k, k') = -\frac{2m}{\hbar^2} \frac{(2\pi)^3}{4\pi} \int d^3r' \frac{e^{-ik'\cdot r'}}{(2\pi)^{3/2}} V(r') \frac{e^{ik\cdot r'}}{(2\pi)^{3/2}} \quad (3.19)$$

$$= -\frac{2m}{\hbar^2} \frac{1}{4\pi} \int d^3r' e^{i(k-k')\cdot r'} V(r') \quad (3.20)$$

With $q = k - k'$ for a spherically symmetric potential, we have:

$$f^{(1)}(k, k') = -\frac{2m}{\hbar^2} \frac{1}{4\pi} \int d^3r' e^{iq \cdot r'} V(r') \quad (3.21)$$

$$= -\frac{1}{2} \frac{2m}{\hbar^2} \int_0^\infty dr r^2 \int_0^\pi \sin(\theta) d\theta e^{iqr \cos(\theta)} V(r) \quad (3.22)$$

$$= -\frac{2m}{\hbar^2} \frac{1}{q} \int_0^\infty dr r V(r) \sin(qr) \quad (3.23)$$

3.2.1 Yukawa Potential

We can't apply the above formula to the Coulomb potential directly since the integral of $\sin(qr)$ is not well defined on an infinite interval. So we instead consider the Yukawa potential:¹⁸

$$V(r) = V_0 \frac{e^{-\mu_2 r}}{\mu_1 r} \quad (3.24)$$

We calculate the scattering amplitude in the first Born approximation:

$$f^{(1)}(k, k') = -\frac{2m}{\hbar^2} \frac{1}{q} \int_0^\infty dr r V_0 \frac{e^{-\mu_2 r}}{\mu_1 r} \sin(qr) \quad (3.25)$$

$$= -\frac{2m}{\hbar^2} \frac{1}{q} \frac{V_0}{\mu_1} \int_0^\infty dr e^{-\mu_2 r} \sin(qr) \quad (3.26)$$

$$= -\frac{2m}{\hbar^2} \frac{1}{q} \frac{V_0}{\mu_1} \frac{1}{2i} \int_0^\infty dr e^{-\mu_2 r} (e^{iqr} - e^{-iqr}) \quad (3.27)$$

$$= -\frac{2m}{\hbar^2} \frac{V_0}{\mu_1} \frac{1}{\mu_2^2 + q^2} \quad (3.28)$$

In the limit of the Coulomb potential:

$$f^{(1)}(k, k') = -\frac{2m}{\hbar^2} \frac{ZZ'e^2}{q^2} \quad (3.29)$$

So the differential cross section is, noting $E_k = \hbar^2 k^2 / 2m$ and $q = 2k \sin(\theta/2)$:

$$\frac{d\sigma}{d\Omega} = \left(\frac{2m}{\hbar^2} \frac{ZZ'e^2}{q^2} \right)^2 \quad (3.30)$$

$$= \frac{1}{16} \frac{Z^2 Z'^2 e^4}{E_k^2} \frac{1}{\sin^4(\theta/2)} \quad (3.31)$$

Which is exactly the result the Rutherford obtained classically for the differential scattering cross section of the Coulomb potential.

Now, an integration of the total scattering cross section diverges for the Coulomb potential, but we can evaluate the total cross section of the Yukawa potential:

$$\sigma = \int d\Omega \frac{d\sigma}{d\Omega} = \left(\frac{2m}{\hbar^2} \frac{V_0}{\mu_1} \right)^2 \int d\Omega \frac{1}{(\mu_2^2 + q^2)^2} \quad (3.32)$$

$$= \left(\frac{2m}{\hbar^2} \frac{V_0}{\mu_1} \right)^2 \int d\Omega \frac{1}{(\mu_2^2 + 4k^2 \sin^2(\theta/2))^2} \quad (3.33)$$

$$= \left(\frac{2m}{\hbar^2} \frac{V_0}{\mu_1} \right)^2 \frac{4\pi}{\mu_2^2 (4k^2 + \mu_2^2)} \quad (3.34)$$

¹⁸As $\mu_2 \rightarrow 0$ and $V_0/\mu_1 \rightarrow ZZ'e^2$ the Yukawa potential becomes the Coulomb potential.

3.2.2 Higher Order Born Approximations

Recall the Lipmann-Schwinger Equation:

$$|\psi_k^{(+)}\rangle = |\phi_k\rangle + \frac{1}{E_k - H_0 + i\epsilon} V |\psi_k^{(+)}\rangle \quad (3.35)$$

Now introduce the transition operator T such that:

$$T|\phi_k\rangle = V|\psi_k^{(+)}\rangle \quad (3.36)$$

Which is equivalent to:

$$T = V + V \frac{1}{E_k - H_0 + i\epsilon} T \quad (3.37)$$

This has an iterative solution. We express $T = \sum_n T^{(n)}$, where $T^{(n)}$ has n of the V operators. For example:

$$T^{(3)} = V \frac{1}{E_k - H_0 + i\epsilon} V \frac{1}{E_k - H_0 + i\epsilon} V \quad (3.38)$$

Now, we notice that the scattering amplitude is:

$$f(k, k') = \sum_{n=1}^{\infty} f^{(n)}(k, k') \quad (3.39)$$

Where:

$$f^{(n)}(k, k') = \langle k' | T^{(n)} | k \rangle \quad (3.40)$$

Keeping n terms of the T operator is known as the n th order Born approximation.

3.3 Partial Wave Approximation

Sakurai 6.4, 6.6

(Valid for strong potentials $V \gg \hbar^2 k^2 / 2m$)

The Laplacian in spherical coordinates is:

$$\nabla^2 f(r, \theta, \varphi) = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial f}{\partial r} \right) + \frac{1}{r^2 \sin(\theta)} \frac{\partial}{\partial \theta} \left(\sin(\theta) \frac{\partial f}{\partial \theta} \right) + \frac{1}{r^2 \sin^2(\theta)} \frac{\partial^2 f}{\partial \varphi^2} \quad (3.41)$$

We note that $H_0 = p^2/2m$ commutes with L and L_z , and we write:

$$H_0 \psi = -\frac{\hbar^2}{2m} \left(\frac{1}{r} \frac{\partial^2}{\partial r^2} (r\psi) \right) + \frac{L^2}{2mr^2} \psi \quad (3.42)$$

Now we can find normalized states $|E\ell m\rangle$ that satisfy:

$$H_0 |E\ell m\rangle = E |E\ell m\rangle \quad (3.43)$$

$$L^2 |E\ell m\rangle = \ell(\ell + 1)\hbar^2 |E\ell m\rangle \quad (3.44)$$

$$L_z |E\ell m\rangle = m\hbar |E\ell m\rangle \quad (3.45)$$

$$\langle r | E\ell m \rangle = R_{E\ell}(r) Y_\ell^m(\theta, \varphi) \quad (3.46)$$

Where $R_{E\ell}$ satisfy:

$$-\frac{\hbar^2}{2m} \left(\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{\ell(\ell+1)}{r^2} \right) R_{E\ell}(r) = ER_{E\ell}(r) \quad (3.47)$$

The solutions $R_{E\ell}$ are the spherical Bessel functions $j_\ell(kr)$ and $n_\ell(kr)$, where k comes from $E = \hbar^2 k^2 / 2m$.

For small x :

$$j_\ell(x) = \frac{x^\ell}{1 \cdot 3 \cdot 5 \cdots (2\ell+1)} \quad (3.48)$$

$$n_\ell(x) = \frac{1 \cdot 3 \cdot 5 \cdots (2\ell+1)}{x^{\ell+1}} \quad (3.49)$$

For large x :

$$j_\ell(x) = \frac{\sin(x - \ell\pi/2)}{x} \quad (3.50)$$

$$n_\ell(x) = \frac{\cos(x - \ell\pi/2)}{x} \quad (3.51)$$

So we find that:

$$\langle r | E \ell m \rangle = \frac{i^\ell}{\hbar} \sqrt{\frac{2mk}{\pi}} j_\ell(kr) Y_\ell^m(\hat{r}) \quad (3.52)$$

$$\langle r | k \rangle = \sum_{\ell, m} \langle r | E \ell m \rangle \frac{\hbar}{\sqrt{mk}} Y_\ell^m(\hat{k})^* \quad (3.53)$$

Thence:

$$\frac{e^{ik \cdot r}}{(2\pi)^{3/2}} = \sum_{\ell} \frac{i^\ell}{(2\pi)^{3/2}} (2\ell+1) P_\ell(\hat{k} \cdot \hat{r}) j_\ell(kr) \quad (3.54)$$

3.3.1 Partial Wave Amplitudes and Phase Shifts

Now, T is a scalar operator, so we can use the Wigner-Eckart Theorem to find:

$$\langle E' \ell' m' | T | E \ell m \rangle = T_{\ell\ell}(E) \delta_{\ell\ell'} \delta_{mm'} \delta(E - E') \quad (3.55)$$

The scattering amplitude is for $f_\ell(k) = -(\pi/k) T_{\ell\ell}(E)$:

$$f(k, k') = -\frac{(2\pi)^3}{4\pi} \frac{2m}{\hbar^2} \langle k' | T | k \rangle \quad (3.56)$$

$$= \sum_{\ell} (2\ell+1) f_\ell(k) P_\ell(\cos(\theta)) \quad (3.57)$$

Additionally, we can show for sufficiently large r that:

$$\langle r | \psi_k^{(+)} \rangle = \frac{1}{(2\pi)^{3/2}} \left[\sum_{\ell} i^\ell (2\ell+1) P_\ell(\cos(\theta)) \frac{e^{i(kr - \ell\pi/2)} - e^{-i(kr - \ell\pi/2)}}{2ikr} + (2\ell+1) f_\ell(k) P_\ell(\cos(\theta)) \frac{e^{ikr}}{r} \right] \quad (3.58)$$

Which amounts to showing that the effect of scattering an incident wave with quantum number ℓ is: $1 \mapsto 1 + 2ikf_\ell(k)$. Now, if we impose unitarity¹⁹, we see that this amounts to a phase shift of δ_ℓ :

$$e^{2i\delta_\ell} = 1 + 2ikf_\ell(k) \quad (3.59)$$

This leads directly to $f_\ell(k) = e^{i\delta_\ell} \sin(\delta_\ell)/k$, and thence:²⁰

$$f(\theta) = \sum_{\ell} (2\ell + 1) e^{i\delta_\ell} \sin(\delta_\ell) P_\ell(\cos(\theta)) \quad (3.61)$$

3.3.2 The Optical Theorem

The total cross section is, using the orthogonality of the Legendre polynomials:

$$\sigma_{\text{tot}} = \int d\Omega |f(\theta)|^2 \quad (3.62)$$

$$= \frac{1}{k^2} \int d\Omega \sum_{\ell, \ell'} (2\ell + 1)(2\ell' + 1) e^{i\delta_\ell} e^{i\delta_{\ell'}} \sin(\delta_\ell) \sin(\delta_{\ell'}) P_\ell(\cos(\theta)) P_{\ell'}(\cos(\theta)) \quad (3.63)$$

$$= \frac{4\pi}{k^2} \sum_{\ell} (2\ell + 1) \sin^2(\delta_\ell) \quad (3.64)$$

Now with cunning, we note:

$$\text{Im}(f(\theta = 0)) = \frac{1}{k} \sum_{\ell} (2\ell + 1) \text{Im}(e^{i\delta_\ell}) \sin(\delta_\ell) P_\ell(\cos(0)) \quad (3.65)$$

$$= \frac{1}{k} \sum_{\ell} (2\ell + 1) \sin^2(\delta_\ell) \quad (3.66)$$

Comparing these results leads us to the Optical Theorem:

$$\sigma_{\text{tot}} = \frac{4\pi}{k} \text{Im}(f(\theta = 0)) \quad (3.67)$$

Which is true even in the absence of rotational symmetry.

3.3.3 Hard Sphere Scattering

We consider scattering from the hard sphere potential:

$$V(r) = \begin{cases} \infty & r < R \\ 0 & R < r \end{cases} \quad (3.68)$$

The general solution outside of the sphere is for constants a_ℓ and b_ℓ :

$$\langle r | \psi \rangle = \sum_{\ell} a_\ell j_\ell(kr) P_\ell(\cos(\theta)) + b_\ell n_\ell(kr) P_\ell(\cos(\theta)) \quad (3.69)$$

¹⁹Physically, this means particles don't accumulate in the scattering region. Mathematically, $|1 + 2ikf_\ell(k)| = 1$.

²⁰In practice phase shifts are calculated by matching boundary conditions, which for potential range R leads to:

$$\tan(\delta_\ell) = \frac{kR j'_\ell(kR) - \beta_\ell j_\ell(kR)}{kR n'_\ell(kR) - \beta_\ell n_\ell(kR)} \quad \text{where} \quad \beta_\ell = kR \left(\frac{j'_\ell(kR) \cos(\delta_\ell) - n'_\ell(kR) \sin(\delta_\ell)}{j_\ell(kR) \cos(\delta_\ell) - n_\ell(kR) \sin(\delta_\ell)} \right) \quad (3.60)$$

Where the boundary condition at $r = R$ leads us to:

$$\tan(\delta_\ell) = \frac{j_\ell(kR)}{n_\ell(kR)} \quad (3.70)$$

Now, taking the low energy limit where $kR \ll 1$, and using Eq. 3.48, we see:

$$\tan(\delta_\ell) = -\frac{(kR)^{2\ell+1}}{(2\ell+1)((2\ell-1)!!)^2} \quad (3.71)$$

Which may be satisfactorily approximated by the $\ell = 0$ term, so we have:

$$\frac{d\sigma}{d\Omega} = \frac{\sin^2(\delta_0)}{k^2} \approx \frac{kR^2}{k^2} = R^2 \quad (3.72)$$

So in this limit we find a total cross section of:

$$\sigma_{\text{tot}} = \int d\Omega \frac{d\sigma}{d\Omega} = 4\pi R^2 \quad (3.73)$$

3.3.4 Ramsauer-Townsend Effect and Bound States

As Sakurai writes: “unless the potential is strong enough to accommodate $\ell \neq 0$ bound states near $E = 0$, the behavior of the radial wavefunction must resemble $j_\ell(kr)$.” So, we consider low energy scattering from a rectangular well or barrier:

$$V(r) = \begin{cases} V_0 & r < R \\ 0 & r > R \end{cases} \quad (3.74)$$

Where $V_0 < 0$ is the attractive potential and $V_0 > 0$ is the repulsive potential.

Matching boundary conditions for the attractive case, we find:

$$k' \cot(k'R) = k \cot(kR + \delta_0) \quad (3.75)$$

Now, if we increase the strength of the potential until $\delta_0 = \pi/2$, the scattering cross section then becomes:

$$\sigma_{\ell=0} = \frac{\sin^2(\delta_0)}{k} = 0 \quad (3.76)$$

This is the Ramsauer-Townsend effect and is observed in the scattering of electrons by noble gases (ex. argon, krypton, and xenon.)

Additionally, for an attractive potential, there may be bound states. For $\kappa = \sqrt{2m(E - V_0)/\hbar^2}$, these states have energy:

$$E_\kappa = \frac{\hbar^2 \kappa^2}{2m} = E - V_0 \approx -|V_0| \quad (3.77)$$

Now if we take the expression in Eq. 3.75, and take the limit of $k \rightarrow 0$ (namely the first term of the taylor expansions), we find:

$$k' \cot(k'R) = \frac{k}{k(R + \delta_0/k)} \quad (3.78)$$

Now, $a = -\delta_0/k$ has units of length, and is in fact called the scattering length, since:

$$\sigma_{\text{tot}} = \frac{4\pi}{k^2} \sum_{\ell=0}^{\infty} (2\ell+1) \sin^2(\delta_\ell) = \frac{4\pi}{k^2} \sin^2(ka) \approx 4\pi a^2 \quad (3.79)$$

3.4 Eikonal Approximation

Sakurai 6.5

Before, we considered the low energy relative to the potential limit: $kR \gg 1$. Now we consider the opposite limit.

We represent the state with action S , where $\hbar \rightarrow 0$ corresponds to the classical limit, by:

$$\psi = \sqrt{\rho(x, t)} e^{iS(x, t)/\hbar} \quad (3.80)$$

1'

Now, we insert this wavefunction into the Schrödinger equation:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V \psi = E \psi \quad (3.81)$$

Or, upon substituting in the state:

$$-\frac{\hbar^2}{2m} \left[\nabla^2 \sqrt{\rho} + \frac{2i}{\hbar} \nabla \sqrt{\rho} \cdot \nabla S - \frac{1}{\hbar^2} \sqrt{\rho} |\nabla S|^2 + \frac{i}{\hbar} \sqrt{\rho} \nabla^2 S \right] + V \sqrt{\rho} = E \sqrt{\rho} = i\hbar \left[\frac{\partial \sqrt{\rho}}{\partial t} + \frac{i}{\hbar} \sqrt{\rho} \frac{\partial S}{\partial t} \right] \quad (3.82)$$

Dropping the terms proportional to \hbar or \hbar^2 , we find the Hamilton-Jacobi equation:

$$\frac{(\nabla S)^2}{2m} + V = -\frac{\partial S}{\partial t} \quad (3.83)$$

For motion along the z -axis with impact parameter b , integrating, we find:

$$\frac{S}{\hbar} = \int_{-\infty}^z d\bar{z} \left[k^2 - \frac{2m}{\hbar^2} V(\sqrt{b^2 + \bar{z}^2}) \right]^{1/2} + \text{constant} \quad (3.84)$$

Where the constant is selected so that $S/\hbar \rightarrow kz$ and $V \rightarrow 0$. So we find that:

$$S(z, b) = kz - \frac{m}{\hbar^2 k} \int_{-\infty}^z d\bar{z} V(\sqrt{b^2 + \bar{z}^2}) \quad (3.85)$$

And substituting into Eq. 3.80, the wave function is:

$$\langle x | \psi_k^{(+)} \rangle = \frac{e^{ikz}}{(2\pi)^{3/2}} \exp \left[-\frac{im}{\hbar^2 k} \int_{-\infty}^z d\bar{z} V(\sqrt{b^2 + \bar{z}^2}) \right] \quad (3.86)$$

Where the scattering amplitude is given by Eq. 3.13:

$$f(k, k') = -\frac{(2\pi)^3}{4\pi} \frac{2m}{\hbar^2} \int d^3x' \frac{e^{ik' \cdot x'}}{(2\pi)^{3/2}} V(x') \langle x' | \psi^{(+)} \rangle \quad (3.87)$$

Should we care to evaluate the scattering cross section for hard-sphere scattering in the Eikonal approximation, we would find that $\sigma_{\text{tot}} = 2\pi R^2$.

4 Miscellaneous Topics

4.1 The Variational Principle

Sakurai 5.4

We may want to find an upper bound on the energy of the ground state of a system. Such an upper bound may be found without determining the ground state wavefunction by use of the variational principle. Theorem: if $|\bar{0}\rangle$ is any state, perhaps an approximation to the ground state eigenfunction $|0\rangle$ of a Hamiltonian H , then:

$$E_{\bar{0}} \equiv \frac{\langle \bar{0} | H | \bar{0} \rangle}{\langle \bar{0} | \bar{0} \rangle} \geq \frac{\langle 0 | H | 0 \rangle}{\langle 0 | 0 \rangle} \equiv E_0 \quad (4.1)$$

Proof sketch: $|\bar{0}\rangle = \sum_{n=0}^N c_n |n\rangle$, so $\langle \bar{0} | H | \bar{0} \rangle = |c_0|^2 \langle 0 | H | 0 \rangle + |c_1|^2 \langle 1 | H | 1 \rangle + \dots$, and since the energies of the excited states ($n \geq 1$) exceed that of the ground state, $\langle n | H | n \rangle > \langle 0 | H | 0 \rangle$, we have $\langle \bar{0} | H | \bar{0} \rangle > \langle 0 | H | 0 \rangle$ (unless $c_0 = 1$ in which case $|\bar{0}\rangle = |0\rangle$).

In practice, the variational method is used by the following procedure:

1. Select a variational ground state wavefunction $|\bar{0}(\lambda)\rangle$, parameterized by a parameter λ
2. Determine $E_{\bar{0}}(\lambda) = \langle \bar{0}(\lambda) | H | \bar{0}(\lambda) \rangle / \langle \bar{0}(\lambda) | \bar{0}(\lambda) \rangle$
3. Find the extremal points where $\partial_{\lambda} E_{\bar{0}}(\lambda) = 0$
4. Determine which extremal point, if any, minimizes the variational ground state energy $E_{\bar{0}}(\lambda)$ —this is the variational upper bound to the ground state energy

As an example, consider an infinite square well described by:

$$V(x) = \begin{cases} 0 & |x| < a \\ \infty & |x| \geq a \end{cases} \quad (4.2)$$

The ground state wavefunction is:

$$|0\rangle = \frac{1}{\sqrt{a}} \cos\left(\frac{\pi}{2a}x\right) \quad (4.3)$$

With energy:

$$E_0 = \frac{\hbar^2}{2m} \frac{\pi^2}{4a^2} \approx 4.9348 \frac{\hbar^2}{4ma^2} \quad (4.4)$$

Now, consider the variational wavefunction (which satisfies the boundary conditions of the well):

$$|\bar{0}(\lambda)\rangle = |a|^\lambda - |x|^\lambda \quad (4.5)$$

Upon summing the kinetic and potential (0) energy, we find:

$$E_{\bar{0}}(\lambda) = \frac{(\lambda+1)(2\lambda+1)}{2\lambda-1} \frac{\hbar^2}{4ma^2} \quad (4.6)$$

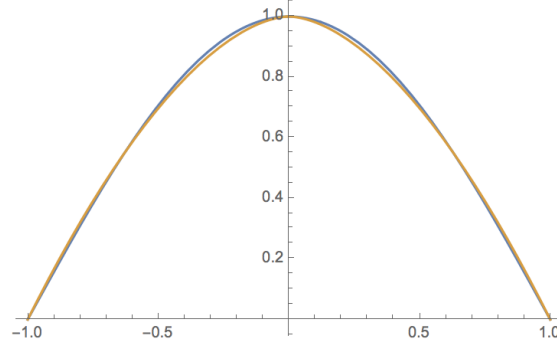
The extremal points are at:

$$\lambda_{\pm} = \frac{1}{2}(1 \pm \sqrt{6}) \quad (4.7)$$

While λ_- corresponds to a lower energy than λ_+ , it does not represent a valid wavefunction since $|\bar{0}(\lambda_-)\rangle|_{x=0} = -\infty$, so we use λ_+ to find the variational energy:

$$E_0(\lambda_+) = \frac{5 + 2\sqrt{6}}{2} \frac{\hbar^2}{4ma^2} \approx 4.9495 \frac{\hbar^2}{4ma^2} \quad (4.8)$$

This is accurate to within 0.3%, and we see that the variational wavefunction (orange) is very close to the exact ground state wavefunction (blue):



4.2 The Geometric Phase

Sakurai 5.6

4.2.1 Sudden and Slow Changes

For systems with sudden changes, the state has no time to evolve even as eigenfunctions change.

Ex. a rectangular box is divided by a thin partition of infinite potential and the partition is suddenly removed. With the sudden change, even if the initial wavefunction is an eigenstate, it has no time to change so it stays the same, and consequently becomes a linear combination of the new eigenstates.

Alternately, systems may change very slowly. In this case if the changes preserve the separation between states, the n th eigenstate of the initial system evolves into the n th eigenstate of the final system provided the eigenstates are gapped. This is the Adiabatic Theorem.

Ex. a rectangular box is gradually extended in the x direction. With the gradual change, eigenstates stay as eigenstates.

4.2.2 The Geometric Phase

Pancharatnam and Longuet-Higgins showed that in addition to the dynamic phase, $\theta_n = -(1/\hbar) \int_0^t dt' E_n(t')$, there is also a geometric phase, γ_n , associated with state evolution. Let the state be, where $c_n(t)$ corresponds to the usual time evolution and $|n(t)\rangle$ corresponds to the changing eigenstates:

$$|\psi(t)\rangle = \sum_n c_n(t) e^{i\theta_n(t)} |n(t)\rangle \quad (4.9)$$

We recall the Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = H(t) |\psi(t)\rangle \quad (4.10)$$

Evaluating the Schrödinger equation, taking care to use the product rule, and applying $\langle m(t)|$, we find:

$$\dot{c}_m(t) = - \sum_n c_n(t) e^{i(\theta_n(t) - \theta_m(t))} \langle m(t) | \partial_t | n(t) \rangle \quad (4.11)$$

From the eigenvalue relation $H(t)|n(t)\rangle = E_n(t)|n(t)\rangle$, we find by differentiating and applying $\langle m(t)|$ that:

$$\langle m(t)|\dot{H}|n(t)\rangle = (E_n(t) - E_m(t))\langle m(t)|\partial_t|n(t)\rangle \quad (4.12)$$

Or:

$$\dot{c}_m(t) = -c_m(t)\langle m(t)|\partial_t|m(t)\rangle - \sum_n c_n(t)e^{i(\theta_n(t)-\theta_m(t))} \frac{\langle m(t)|\dot{H}|n(t)\rangle}{E_n - E_m} \quad (4.13)$$

In the adiabatic approximation where $\langle m(t)|\dot{H}|n(t)\rangle/(E_n - E_m) \ll E_m/\hbar$, we have:

$$\dot{c}_m(t) = -c_m(t)\langle m(t)|\partial_t|m(t)\rangle \quad (4.14)$$

Which leads us to an expression for geometric phase factor (which like θ_n is a real number):

$$\gamma_n(t) = i \int_0^t dt' \langle n(t')|\partial_{t'}|n(t')\rangle \quad (4.15)$$

Where:

$$c_n(t) = e^{i\gamma_n(t)}c_n(0) \quad (4.16)$$

So we have:

$$|\psi(t)\rangle = \sum_n c_n(t)e^{i\gamma_n(t)}e^{i\theta_n(t)}|n(t)\rangle \quad (4.17)$$

Whose use is limited by our knowledge of $|n(t)\rangle$.

4.2.3 Berry's Method for Calculating the Geometric Phase

Berry showed²¹ that for a system that evolves around a closed loop, if we assume the time dependence of the Hamiltonian is represented by a vector of parameters $R(t)$, then:

$$\langle n(t)|\partial_t|n(t)\rangle = \langle n(t)|\nabla_R|n(t)\rangle \cdot \frac{dR}{dt} \quad (4.18)$$

Thence, through a change of variables, integrating around a closed loop l :

$$\gamma_n(l) = i \oint_l \langle n(t)|\nabla_R|n(t)\rangle \cdot dR \quad (4.19)$$

Letting $A_n(R) = i\langle n(t)|\nabla_R|n(t)\rangle$, and using Stokes theorem, we find the line integral around the loop is equal to an area integral over the enclosed surface:

$$\gamma_n(l) = \oint_l A_n(R) \cdot dR = \int (\nabla_R \times A_n(R)) \cdot da \quad (4.20)$$

Evidently, $B_n(R) = \nabla_R \times A_n(R)$ is a flux, and we see that the geometric phase $\gamma_n(l)$ is the same for all closed loops that encompasses the same total flux. In fact, even if we introduce an arbitrary phase factor $|n(t)\rangle \mapsto e^{i\delta(R)}|n(t)\rangle$, γ_n is unchanged. So γ_n only depends on the flux enclosed by the path.

Combining the results above and simplifying, the geometric phase can be calculated using the identities:

$$\gamma_n(l) = \int B_n(R) \cdot da \quad (4.21)$$

$$B_n(R) = i \sum_{m \neq n} \frac{\langle n(t)|\nabla_R H|m(t)\rangle \times \langle m(t)|\nabla_R H|n(t)\rangle}{(E_n - E_m)^2} \quad (4.22)$$

²¹M. V. Berry, *Quantal Phase Factors Accompanying Adiabatic Changes*, Proc. Roy. Soc. (London), **A392** (1984).

Appendix A Review of Electromagnetic Waves

Maxwell's equations are:

$$\nabla \cdot E = 4\pi\rho \quad (\text{A.1})$$

$$\nabla \times E = -\frac{1}{c} \frac{\partial B}{\partial t} \quad (\text{A.2})$$

$$\nabla \cdot B = 0 \quad (\text{A.3})$$

$$\nabla \times B = \frac{4\pi}{c} I + \frac{1}{c} \frac{\partial E}{\partial t} \quad (\text{A.4})$$

In the absence of currents and charge distributions:

$$\nabla \cdot E = 0 \quad (\text{A.5})$$

$$\nabla \times E = -\frac{1}{c} \frac{\partial B}{\partial t} \quad (\text{A.6})$$

$$\nabla \cdot B = 0 \quad (\text{A.7})$$

$$\nabla \times B = \frac{1}{c} \frac{\partial E}{\partial t} \quad (\text{A.8})$$

Which lead to the wave equations for $f \in \{E, B\}$:

$$\nabla^2 f = \frac{1}{c^2} \frac{\partial^2 f}{\partial t^2} \quad (\text{A.9})$$

We consider the solutions that are monochromatic plane waves with linear polarization $\hat{\varepsilon}$ and direction of propagation \hat{n} , with $\hat{\varepsilon}_E \cdot k = \hat{\varepsilon}_B \cdot k = 0$ and $k \times \hat{\varepsilon}_E = |k| \hat{\varepsilon}_B$, for $k = |k| \hat{n}$ and $|k| = \omega/c$:

$$E = E_0 e^{i(k \cdot x - \omega t)} \hat{\varepsilon}_E \quad (\text{A.10})$$

$$B = B_0 e^{i(k \cdot x - \omega t)} \hat{\varepsilon}_B \quad (\text{A.11})$$

We can also express this in terms of the vector potential, where $B = \nabla \times A$, and with $\phi = 0$, $E = -(1/c) \partial_t A$:

$$A = A_0 \left[e^{i(k \cdot x - \omega t)} + e^{-i(k \cdot x - \omega t)} \right] \hat{\varepsilon} \quad (\text{A.12})$$

The Hamiltonian for this system is:

$$H(t) = \frac{1}{2m} (p - (e/c)A)^2 + e\phi(x) \quad (\text{A.13})$$

$$= \frac{p^2}{2m} - \frac{e}{2mc} (A \cdot p + p \cdot A) + \frac{e^2}{2mc^2} |A|^2 + e\phi(x) \quad (\text{A.14})$$

We have $\phi(x) = 0$. Since $k \cdot A = 0$ and $\nabla \cdot A = 0$, $A \cdot p = p \cdot A$ and we can neglect the $|A|^2$ term. So we have:

$$H(t) = \frac{p^2}{2m} - \frac{e}{mc} A \cdot p \quad (\text{A.15})$$

Which is ripe for the application of time-dependent perturbation theory.

Appendix B Review of Complex Line Integrals

A function $f(z)$ is analytic on a domain D iff it has a Laurent series (power series with negative terms) that converges on D :

$$f(z) = \sum_{n=-\infty}^{\infty} a_n z^n \quad (\text{B.1})$$

The residue of a function $f(z)$ at z_0 is:²²

$$\text{Res}[f(z), z_0] = a_{-1} \quad (\text{B.2})$$

Rule 1: if $f(z)$ is non-zero and analytic at z_0 , then:

$$\text{Res} \left[\frac{f(z)}{(z - z_0)^n}, z_0 \right] = \frac{f^{(n-1)}(z_0)}{(n-1)!} \quad (\text{B.3})$$

Rule 2: if $f(z)$ and $g(z)$ are analytic at z_0 and if $g(z)$ has a simple zero²³ at z_0 , then:

$$\text{Res} \left[\frac{f(z)}{g(z)}, z_0 \right] = \frac{f(z)}{g'(z)} \quad (\text{B.4})$$

The Residue Theorem states that for any (counter-clockwise oriented) closed loop γ in which there are a set of isolated singularities $\{z_j\}$, the line integral around γ is:

$$\oint_{\gamma} f(z) dz = 2\pi i \sum_j \text{Res}[f(z), z_j] \quad (\text{B.5})$$

A useful form of the Residue Theorem is the Cauchy Integral Formula. If $f(z)$ is analytic at z_0 , then for any (counter-clockwise oriented) closed loop γ that encloses z_0 :

$$f(z_0) = \frac{1}{2\pi i} \oint_{\gamma} \frac{f(z)}{z - z_0} dz \quad (\text{B.6})$$

More generally:

$$f^{(n)}(z_0) = \frac{n!}{2\pi i} \oint_{\gamma} \frac{f(z)}{(z - z_0)^{n+1}} dz \quad (\text{B.7})$$

Now, suppose that we define a loop γ as a semicircle in the upper half plane bounded by the interval $[-R, R]$. If there are singularities, $\{z_j\}$, in the loop, a line integral around the loop will accumulate their residues, while in many cases it can be shown that the line integral along the arc is zero as $R \rightarrow \infty$. This allows us to compute integrals along the real line using the Residue Theorem. In particular, if $P(x)$ and $Q(x)$ are polynomials and $\deg(Q) \geq \deg(P) + 2$, then:

$$\int_{-\infty}^{\infty} dx \frac{P(x)}{Q(x)} = 2\pi i \sum_j \text{Res} \left[\frac{P(z)}{Q(z)}, z_j \right] \quad (\text{B.8})$$

For the same requirements, we have for real $k > 0$:

$$\int_{-\infty}^{\infty} dx \frac{P(x)}{Q(x)} e^{ikx} = \frac{2\pi i}{e^k} \sum_j \text{Res} \left[\frac{P(z)}{Q(z)}, z_j \right] \quad (\text{B.9})$$

²²Residues can be evaluated by WolframAlpha and Mathematica using `Residue[f[z], {z, z0}]`.

²³A zero of $f(z)$ at z_0 is simple iff $f'(z_0) \neq 0$.