Summary of Formulae in Quantum Mechanics

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 $Abbreviations: \ CM = Classical\ Mechanics,\ QM = Quantum\ Mechanics,\ CR = commutation\ relation,\ SE = Schr\"{o}dinger\ equation,\ TISE = time-independent\ Schr\"{o}dinger\ equation$

1 Wave Mechanics

Main idea: System is described by a \mathbb{C} -valued wavefunction $\psi(x,t)$. Time evolution is described by the *Time-dependent Schrödinger* equation:

$$i\hbar\partial_t\psi=H\psi=-\frac{\hbar^2}{2m}\nabla^2\psi+V(x)\psi \tag{1}$$

Separation of variables $\psi(x,t)=e^{-iEt}\chi(x)$ gives Time-independent Schrödinger equation (TISE):

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

These equations are linear, and in fact QM is entirely linear. The *superposition principle* says if ψ , ϕ are states, so is $a\psi + b\phi$ for $a,b\in\mathbb{C}$. The space of wavefunctions is given the inner product

$$\langle \phi, \psi \rangle = \int_{\mathbb{R}} \overline{\phi(x)} \psi(x) \, dx;$$
 (3)

 ψ is normalised if $\langle \psi, \psi \rangle = 1$.

1.1 Probability

If the system is in the state with wavefunction ψ , the probability that we measure it to be in the state with wavefunction ϕ is

$$\frac{\left|\langle\phi,\psi\rangle\right|^2}{\langle\phi,\phi\rangle\langle\psi,\psi\rangle}$$

Given this, the overall phase of the wavefunction has no physical impact. The probability of finding the particle in an infinitesimal interval dx is $\frac{|\psi(x)|^2}{\langle \psi, \psi \rangle} dx = \rho(x) dx$. The probability density ρ satisfies the *continuity equation*

$$\partial_t \rho + \nabla \cdot \mathbf{j} = 0, \tag{4}$$

where \mathbf{j} is the *probability current*

$$\mathbf{j} = \frac{\hbar}{2im} \left(\overline{\psi} \nabla \psi - \psi \nabla \overline{\psi} \right) = \frac{\hbar}{m} \Im(\overline{\psi} \nabla \psi). \tag{5}$$

1.2 Plane Wave and Wavepacket

SE for a free particle is

$$i\hbar\partial_t\psi = -\frac{\hbar^2}{2m}\nabla^2\psi. \tag{6}$$

A (non-normalisable) solution is

$$\psi(\mathbf{x}, t) = \exp\left(i\mathbf{k} \cdot \mathbf{x} - i\omega t\right),\tag{7}$$

with $\omega = \hbar k^2/(2m)$. Interpreted as a particle beam or a *plane wave*. The *de Broglie relations* for a matter wave are

$$E = \hbar \omega, \quad \mathbf{p} = \hbar \mathbf{k}.$$
 (8)

These imply that this is an energy eigenstate with $E = p^2/(2m)$, as we expect classically.

Given a Gaussian initial state $\psi(x,0)=(a\pi)^{-1/4}e^{-x^2/(2a)}$, one finds that it evolves into

$$\psi(x,t) = \left(\frac{a}{\pi}\right)^{1/4} \frac{1}{\sqrt{a + i\hbar t/m}} \exp\left(-\frac{x^2}{2(a + i\hbar t/m)}\right). \tag{9}$$

1.3 Galilean Transformation

Given a solution $\Psi(x,t)$, we can consider a Galilean transformation $t'=t, \, x'=x-ut$. Then looking for solutions of the form $\Psi(x-ut,t)e^{i\alpha(x,t)}$, which all have the same probability density, we find

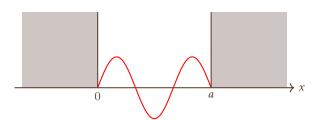
$$\Psi(x - ut, t)e^{im(ux - u^2t/2)/\hbar} \tag{10}$$

is also a solution.

2 Example Potentials

A normalisable solution of the TISE with a given V is called a *bound state* of V. In this section we find the bound states of some simple potentials.

2.1 Infinite Square Well



$$V(x) = \begin{cases} 0 & 0 \le x \le a \\ \infty & \text{else} \end{cases} \tag{11}$$

Outside [0, a], wavefunction must be zero (or TISE makes no sense). Inside, have

$$-\frac{\hbar^2}{2m}\chi^{\prime\prime} = E\chi,\tag{12}$$

which is solved by $\chi(x) = A \sin kx + B \cos kx$, $k = 2mE/\hbar^2$. Continuity of χ at $x = 0 \implies B = 0$, and continuity at $x = a \implies k = 0, \pi/a, 2\pi/a, \dots$ Hence energy levels are

$$E_n = \frac{n^2 \hbar^2 \pi^2}{2ma^2}, \quad n = 1, 2, \cdots$$
 (13)

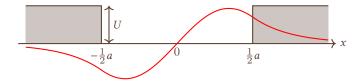
with normalised eigenfunctions (note can't have n=0 to have a normalisable wavefunction)

$$\chi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right). \tag{14}$$

This is the easiest way, but one may also look at odd and even solutions in the symmetric box on [-a/2, a/2].

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2.2 Finite Square Well



$$V(x) = \begin{cases} 0 & -a/2 \le x \le a/2 \\ U & \text{else} \end{cases}$$
 (15)

Outside, have

$$-\frac{\hbar^2}{2m}\chi^{\prime\prime} = (E - V)\chi\tag{16}$$

Need exponential decay here to be normalisable, so take $2m(E-U)/\hbar^2 = -\alpha^2 < 0$. We assume that $\alpha, k > 0$. Potential is unchanged under parity $P: x \mapsto -x$, so can look solutions with definite parity: even and odd.

Even Solution has form

$$\chi(x) = \begin{cases} Ae^{\lambda(x+a/2)} & x < -a/2 \\ B\cos kx & |x| \le a/2 \\ Ae^{-\lambda(x-a/2)} & x > a/2 \end{cases}$$
 (17)

Continuity of χ , χ' at x = a/2 gives

$$A - B\cos\frac{1}{2}ka = 0$$
$$-\lambda A + kB\sin\frac{1}{2}ka = 0.$$
 (18)

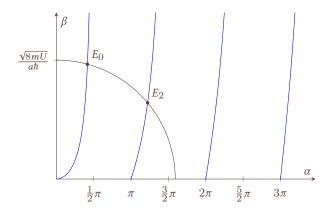
If we write this as a matrix equation for A, B, to have a nonzero solution to the original equations, we need the determinant to vanish. This gives

$$k\sin\frac{1}{2}ka - \lambda\cos\frac{1}{2}ka = 0. \tag{19}$$

So have two conditions on k and λ . Writing $\alpha = ka/2$, $\beta = \lambda a/2$, we have

$$\beta = \alpha \tan \alpha, \quad \alpha^2 + \beta^2 = \frac{8mU}{a^2\hbar^2} \tag{20}$$

Plotting both of these conditions shows that there is always a solution. Taking $U \to \infty$ recovers the infinite well's even solutions.



Odd Solution has form

$$\chi(x) = \begin{cases} -Ae^{-\lambda(x-a/2)} & x < -a/2 \\ B\sin kx & |x| \le a/2 \\ Ae^{-\lambda(x-a/2)} & x > a/2 \end{cases}$$
 (21)

Continuity of χ , χ' at x = a/2 gives

$$A - B\sin\frac{1}{2}ka = 0$$

$$-\lambda A - kB\cos\frac{1}{2}ka = 0.$$
(22)

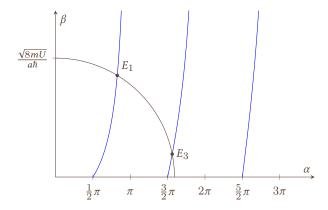
If we write this as a matrix equation for A, B, to have a nonzero solution to the original equations, we need the determinant to vanish. This gives

$$-k\cos\frac{1}{2}ka - \lambda\sin\frac{1}{2}ka = 0. \tag{23}$$

Again have two conditions on k and λ . In the same notation as above, we have

$$\beta = -\alpha \cot \alpha, \quad \alpha^2 + \beta^2 = \frac{8mU}{a^2\hbar^2} \tag{24}$$

Now, there is only a solution if $32mU/a^2\hbar^2\pi^2 \geqslant 1$. Again, taking $U \to \infty$ recovers the infinite well's odd solutions.



So the system has a finite number of bound states, with energies satisfying the inequalities

$$\frac{n^2\hbar^2\pi^2}{2ma^2} < E_n < \frac{(n+1)^2\hbar^2\pi^2}{2ma^2}.$$
 (25)

3 Harmonic Oscillator

TISE is

$$-\frac{\hbar^2}{2m}\chi^{\prime\prime} + \frac{1}{2}m\omega^2 x^2 \chi = E\chi. \tag{26}$$

Nondimensional change of variables $y=\sqrt{m\omega/\hbar}x,\,\mathcal{E}=2E/(\hbar\omega)$ gives

$$-\frac{d^2\chi}{dx^2} + y^2\chi = \mathcal{E}\chi. \tag{27}$$

If $\mathcal{E}=1$, has solution $\chi_0(y)=e^{-y^2/2}$. Expect all solutions to act like this due to dominance of $y^2\chi$ term. Substituting $\chi(y)=f(y)e^{-y^2/2}$, find the *Hermite equation*,

$$\frac{d^2f}{dy^2} - 2y\frac{df}{dy} + (\mathcal{E} - 1)f = 0.$$
 (28)

Method of Frobenius gives either nonterminating series that are asymptotic to e^{y^2} as $|y| \to \infty$, or if $\mathcal{E} = 2n+1, n=0,1,\ldots$, the Hermite polynomial of degree n. Hence the bound-state energies are $E_n = (n+1/2)\hbar\omega$, and the corresponding normalised eigenstates are

$$\chi_n(y) = \frac{\pi^{-1/4}}{\sqrt{2^n n!}} H_n(y) e^{-y^2/2}.$$
 (29)

4 Scattering

Suppose V(x)=0 outside [0,a]. We again take k>0, $k^2=2mE/\hbar^2$. We look for solutions of the form

$$\psi(x) = \begin{cases} Ie^{ikx} + Te^{-ikx} & x < 0 \\ Re^{ikx} & x > a \end{cases}$$
 (30)

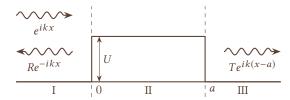
Scatter a wave of amplitude *I. R* is *reflexion coefficient, T* is *scattering coefficient.* For 1D solutions, probability current is constant

since no ψ' term in TISE. Calculating current in both regions gives

$$|I|^2 = |R|^2 + |T|^2. (31)$$

Interpret $|R/I|^2$ as reflexion probability, $|T/I|^2$ as transmission probability.

4.1 Example: Square Barrier



$$V(x) = \begin{cases} U & 0 < x < a \\ 0 & \text{else} \end{cases}$$
 (32)

We choose the solution between 0 and *a* carefully:

$$\psi(x) = \begin{cases} Ie^{ikx} + Te^{-ikx} & x < 0 \\ A\cos\lambda(x-a) + B\frac{1}{\lambda}\sin\lambda(x-a) & 0 \le x \le a \\ Re^{ik(x-a)} & x > a \end{cases}$$
(33)

Continuity of ψ , ψ' at x = 0, a gives four equations:

$$I + T = A\cos \lambda a - B\frac{1}{\lambda}\sin \lambda a$$

$$ik(I - T) = A\sin \lambda a + B\cos \lambda a$$

$$A = R$$

$$B = ikR$$
(34)

Solving these give the reflection and transmission coefficients, which are too messy to give here.

5 Operators

Operators are linear functions on the space of states (endomorphisms). Examples:

Position is "multiply by x"

Momentum is $\mathbf{p} = -i\hbar\nabla$

Energy is the Hamiltonian, $H = \frac{1}{2m}p^2 + V$.

Parity is P, Pf(x) = f(-x).

The *expected value* of an operator A in state ψ is

$$\langle A \rangle_{\psi} = \frac{\langle \psi, A\psi \rangle}{\langle \psi, \psi \rangle}.$$
 (35)

The *uncertainty* or variance of an operator in state ψ

$$(\Delta A)_{\psi}^{2} = \langle (A - \langle A \rangle_{\psi})^{2} \rangle_{\psi} = \langle A^{2} \rangle_{\psi} - \langle A \rangle_{\psi}^{2}. \tag{36}$$

Operators do not in general commute: $AB \neq BA$. The *commutator* is a product that measures this: given A, B, their commutator is the operator

$$[A, B] = AB - BA. \tag{37}$$

This has the following properties:

1. Linear: $[\lambda A + \mu B, C] = \lambda [A, C] + \mu [B, C]$

2. Antisymmetric: [A, A] = 0, so [A, B] = -[B, A]

3. Leibniz: [A, BC] = B[A, C] + [A, B]C.

The basic commutator in quantum mechanics is

$$[x, p] = i\hbar. (38)$$

5.1 Eigenvalues and Eigenstates

If $\psi \neq 0$ and

$$A\psi = \lambda\psi,\tag{39}$$

 λ is called an *eigenvalue*, ψ the corresponding *eigenstate*. When we solve TISE, we find eigenvalues and eigenstates of H.

We have the usual results: for Hermitian operators,

- 1. Eigenvalues are real,
- 2. Eigenstates with different eigenvalues are orthogonal.
- We also assume that the normalised eigenstates span the space of wavefunctions, so we can write

$$\psi = \sum_{\lambda,n} \langle e_{\lambda,n}, \psi \rangle e_{\lambda,n} \tag{40}$$

with $e_{\lambda, n}$ the normalised eigenstates with eigenvalue λ .

A and B have simultaneous eigenstates (that is, ψ satisfying $A\psi = \lambda\psi$, $B\psi = \mu\psi$) if and only if [A,B] = 0.

5.2 Uncertainty Principle

If two operators do not commute, we cannot expect to measure both exactly. This is quantified in an *uncertainty principle*: Let A, B be Hermitian. Then taking $C = A + i\lambda B$, $\lambda \in \mathbb{R}$,

$$C^{\dagger}C = A^2 + \lambda^2 B^2 + \lambda i [A, B]. \tag{41}$$

The first three are Hermitian, so i[A, B] is also Hermitian. We have

$$\begin{split} 0 & \leq \langle C\psi, C\psi \rangle = \langle \psi, C^{\dagger}C\psi \rangle \\ & = \langle A^2 \rangle_{\psi} + \lambda^2 \langle B^2 \rangle_{\psi} + \lambda \langle i[A, B] \rangle_{\psi} \,. \end{split}$$

For this to always be nonnegative, can have at most one real root, so discriminant gives

$$\langle A^2 \rangle_{\psi} \langle B^2 \rangle_{\psi} \geqslant \frac{1}{4} (\langle i[A, B] \rangle_{\psi})^2.$$
 (42)

This works for any A, B, so if we apply it to $\tilde{A} = A - \langle A \rangle_{\psi}$ and $\tilde{B} = B - \langle B \rangle_{\psi}$, we find $[\tilde{A}, \tilde{B}] = [A, B]$ and hence

$$(\Delta A)_{\psi}(\Delta B)_{\psi} \geqslant \frac{1}{2} \left| \langle [A, B] \rangle_{\psi} \right|. \tag{43}$$

Most famous is Heisenberg's uncertainty principle,

$$(\Delta x)(\Delta p) \geqslant \frac{1}{2}\hbar. \tag{44}$$

5.3 Ehrenfest and Heisenberg

We can determine the time evolution of the expectation of an operator using the SE:

$$\begin{split} \frac{d}{dt}\langle A\rangle_{\psi} &= \frac{d}{dt} \int \overline{\psi} A\psi = \int (\overline{\partial_t \psi} A\psi + \overline{\psi} A \partial_t \psi + \overline{\psi} (\partial_t A) \psi) \\ &= \langle \partial_t \psi, A\psi \rangle + \langle \psi, A \partial_t \psi \rangle + \langle \partial_t A \rangle_{\psi} \\ &= \langle \frac{1}{i\hbar} H\psi, A\psi \rangle + \langle \psi, A \frac{1}{i\hbar} H\psi \rangle + \langle \partial_t A \rangle_{\psi} \\ &= \frac{1}{i\hbar} \langle [A, H] \rangle_{\psi(t)} + \langle \partial_t A \rangle_{\psi} \end{split}$$

Two specific examples are \mathbf{x} and \mathbf{p} : we have

$$\frac{d}{dt}\langle \mathbf{x}\rangle_{\psi} = \frac{1}{i\hbar}\langle [\mathbf{x}, H]\rangle_{\psi} = \frac{1}{2mi\hbar}\langle [\mathbf{x}, p^2]\rangle_{\psi} = \frac{1}{m}\langle \mathbf{p}\rangle_{\psi}$$
(45)

$$\frac{d}{dt}\langle \mathbf{p} \rangle_{\psi} = \frac{1}{i\hbar} \langle [\mathbf{x}, H] \rangle_{\psi} = \langle [\mathbf{p}, V(x)] \rangle_{\psi} = \langle -\nabla V \rangle_{\psi}. \tag{46}$$

6 Postulates of Quantum Mechanics

States The state of the system is described by vector ψ in a Hilbert space \mathcal{H} .

Observables To each observable quantity A (position, momentum, angular momentum, energy, charge, parity, &c.) there corresponds a Hermitian operator \hat{A} acting on \mathcal{H} , although we write A for both.

Probability The probability of measuring ψ as being in state ϕ is $|\langle \phi, \psi \rangle|^2 / \langle \phi, \phi \rangle \langle \psi, \psi \rangle$. After the system is measured to be in state ϕ , it remains in ϕ . In particular, the only measureable values of an observable A are given by the eigenvalues of the operator \hat{A} ; when we measure A has value a, state of system becomes an eigenstate of \hat{A} with eigenvalue a.

Average The expected value of \hat{A} in state ψ is $\langle \psi, \hat{A}\psi \rangle / \langle \psi, \psi \rangle$.

Time evolution The vector evolves via the Schrödinger equation. $i\hbar\partial_t\psi=H\psi.$

7 Three Dimensions

(In this section we use Einstein summation convention throughout.)

In 3D, CRs between position and momentum are

$$[x_i, x_j] = 0, \quad [p_i, p_j] = 0, \quad [x_i, p_j] = i\hbar \delta_{ij}.$$

7.1 Angular Momentum

CM angular momentum is defined as

$$L_i = (\mathbf{x} \times \mathbf{p})_i = \varepsilon_{ijk} x_j p_k. \tag{47}$$

This contains no x_ip_i terms, so order of operators does not matter and we take this as QM definition. Components satisfy the CRs

$$[L_i, L_j] = i\hbar \varepsilon_{ijk} L_k. \tag{48}$$

OTOH, the total angular momentum $L^2 = L_i L_i$ commutes with the individual components:

$$[L^2, L_i] = 0, (49)$$

so can find simultaneous eigenfunctions of L^2 and L_2 (spherical harmonics, § 7.3).

7.2 Radial Potentials

The relationship between p^2 and L^2 is

$$p^{2} = -\hbar^{2} \nabla^{2} = -\hbar^{2} \frac{1}{r} \partial_{r}^{2} r + \frac{L^{2}}{r^{2}},$$
 (50)

so

$$L^{2} = \frac{1}{\sin \theta} \partial_{\theta} \sin \theta \, \partial_{\theta} + \frac{1}{\sin^{2} \theta} \partial_{\varphi}^{2}, \quad L_{3} = -i\hbar \partial_{\varphi}. \tag{51}$$

If V=V(r), can separate variables in TISE as $\chi(r,\theta,\varphi)=R(r)Y(\theta,\varphi)$. Then iff $L^2Y=\hbar^2\ell(\ell+1)Y$, have radial equation

$$-\frac{\hbar^2}{2\mu}\frac{1}{r}\partial_r^2 rR + \left(V(r) + \frac{\hbar^2\ell(\ell+1)}{r^2}\right)R = ER. \tag{52}$$

Writing $\chi = rR$ turns this into a 1D TISE with modified potential,

$$-\frac{\hbar^2}{2\mu}\chi^{\prime\prime} + \left(V(r) + \frac{\hbar^2\ell(\ell+1)}{r^2}\right)\chi = E\chi, \tag{53}$$

where χ is must be odd so R is regular at r = 0.

Thus a sufficiently shallow 3D finite spherical well has no bound state.

7.3 Spherical Harmonics

Spherical harmonics $Y_{\ell}^{m}(\theta, \varphi)$ are simultaneous eigenfunctions of L^{2} and L_{2} :

$$L^{2}Y_{\ell}^{m} = \hbar^{2}\ell(\ell+1)Y_{\ell}^{m}, \quad L_{3}Y_{\ell}^{m} = \hbar mY_{\ell}^{m}.$$
 (54)

Separating variables gives

$$-\frac{1}{\sin \theta} \left(\sin \theta \Theta'(\theta) \right)' + \frac{m^2}{\sin^2 \theta} \Theta(\theta) = \ell(\ell+1)\Theta(\theta)$$
 (55)

$$-i\Phi' = m\Phi. \tag{56}$$

Φ equation gives $\Phi(\varphi) = e^{im\varphi}$. m must be an integer for this to be continuous. Changing variables $x = \cos \theta$ in the Θ equation, then $\frac{d}{dx} = \sin \theta \frac{d}{d\theta}$, so

$$-((1-x^2)\Theta'(x))' + \frac{m^2}{1-x^2}\Theta(x) = \ell(\ell+1)\Theta(x),$$

the associated Legendre equation. The spherical harmonics are thus

$$Y_{\ell}^{m}(\theta,\phi) = \sqrt{\frac{2\ell+1}{4\pi} \frac{(\ell-m)!}{(\ell+m)!}} P_{\ell}^{m}(\cos\theta) e^{im\varphi}, \tag{57}$$

where $\ell \in \{0, 1, 2, \dots\}, m \in \{-\ell, -\ell + 1, \dots, \ell\}.$

They are normalised so

$$\int_{0}^{2\pi} \int_{0}^{\pi} \overline{Y_{\ell}^{m}(\theta, \varphi)} Y_{\ell'}^{m'}(\theta, \varphi) \sin \theta \, d\theta \, d\phi = \delta_{\ell\ell'} \delta_{mm'} \tag{58}$$

8 Hydrogen Atom

Here have potential

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}. (59)$$

Making non-dimensional substitution $y=r/r_0,\, v^2=-2mE/\hbar^2$, where $r_0=4\pi\varepsilon_0\hbar^2/(m_ee^2)$ is the Bohr radius, TISE becomes

$$-\frac{1}{y}\left(\frac{d}{dy}\right)^2 yR + \left(\frac{\ell(\ell+1)}{y^2} - \frac{2}{y}\right)R = -v^2R. \tag{60}$$

For large y, equation looks like $R'' = -v^2 R$, so normalisable solution looks like e^{-vy} . For small y, equation looks like $(yR)'' = \ell(\ell+1)/y$, which has solutions y^ℓ and $y^{-\ell-1}$. Choosing regular one, and making the substitution $R(y) = y^\ell e^{-vy} f(y)$, equation becomes

$$yf'' + ((2\ell+1) + 1 - 2\nu y)f' + 2(1 - (\ell+1)\nu)f = 0.$$
 (61)

Changing variables to $\rho = 2vy$ gives

$$\rho f'' + ((2\ell + 1) + 1 - \rho)f + 2(v^{-1} - \ell - 1)f,$$

the associated Legendre equation with $\alpha = 2\ell + 1$, $n = v^{-1} - \ell - 1$. Has normalisable polynomial solutions when $\nu = (n+\ell)^{-1}$, $n = 1, 2, \ldots$ Energy levels are

$$E_N = -\frac{\hbar^2}{2\mu r_0^2 (n+\ell)^2} = -\frac{\mu e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \frac{1}{N^2},$$
 (62)

and corresponding eigenfunctions are

$$\chi_{n\ell m}(x) = \sqrt{\left(\frac{2}{nr_0}\right)^3 \frac{(n-\ell-1)!}{2n(n+\ell)!}} \rho^{\ell} L_{n-\ell-1}^{2\ell+1}(\rho) e^{-\rho/2} Y_{\ell}^m(\theta, \varphi), \tag{63}$$

where $N = n + \ell \in \{1, 2, ...\}$, $\ell \in \{0, 1, ..., N - 1\}$ and $m \in \{-\ell, -\ell + 1, ..., \ell\}$. Degeneracy of Nth level is N^2 .