Summary of Formulae in Quantum Mechanics

Richard Chapling

v1.2 1 May 2023

Abbreviations: CM = Classical Mechanics, QM = Quantum Mechanics, CR = commutation relation, SE = Schrödinger equation, TISE = time-independent Schrödinger 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* (SE):

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

This is first-order in time, so only need $\psi(x,0)$ to determine subsequent behaviour.

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

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

If V has at worst a finite jump at a point, ψ, ψ' are continuous there.

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

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

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

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

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

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

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

$$E = \hbar\omega, \qquad \mathbf{p} = \hbar\mathbf{k}. \tag{8}$$

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

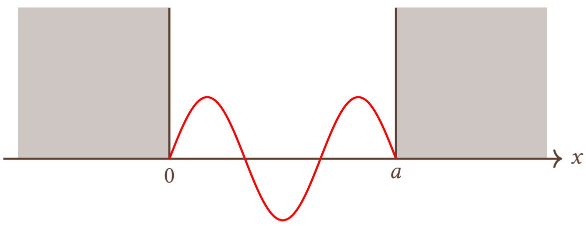
$$\Psi(x-ut,t)e^{im(ux-u^2t/2)/\hbar} \tag{10}$$

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



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

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

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

which is solved by $\chi(x) = A\sin kx + B\cos kx$, $k^2 = 2mE/\hbar^2$. 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

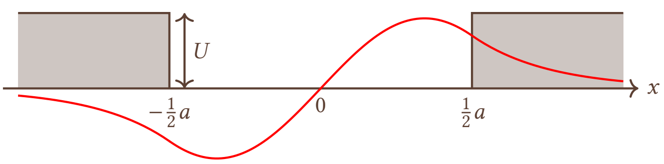
$$E_n = \frac{n^2\hbar^2\pi^2}{2ma^2}, \qquad n = 1, 2, \cdots \tag{13}$$

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 $[-a/2, a/2]$.

2.2 Finite Square Well



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

Outside, have

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

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

Even Solution has form

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

Continuity of χ, χ' at $x = a/2$ gives

$$\begin{aligned} A - B\cos\tfrac{1}{2}ka &= 0 \\ -\lambda A + kB\sin\tfrac{1}{2}ka &= 0. \end{aligned} \tag{18}$$

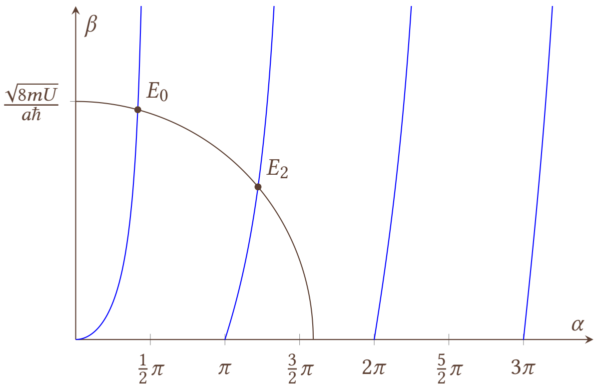
If we write this as a matrix equation for A, B, to have a nonzero solution to the original equations, we need the determinant to vanish. This gives

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

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

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

Continuity of χ, χ' at $x = a/2$ gives

$$\begin{aligned} A - B\sin\tfrac{1}{2}ka &= 0 \\ -\lambda A - kB\cos\tfrac{1}{2}ka &= 0. \end{aligned} \tag{22}$$

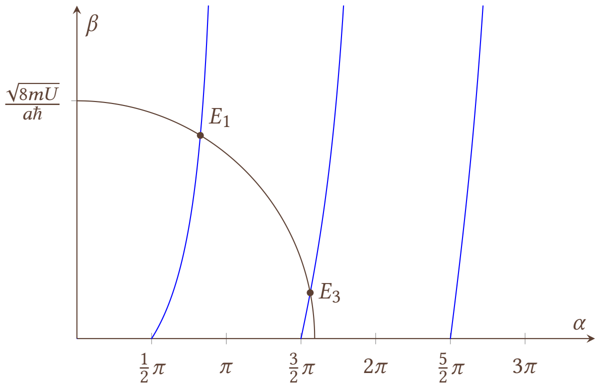
If we write this as a matrix equation for A, B, to have a nonzero solution to the original equations, we need the determinant to vanish. This gives

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

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

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

3 Harmonic Oscillator

TISE is

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

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*,

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

Method of Frobenius gives either nonterminating series that are asymptotic to e^{y^2} as $|y| \to \infty$, or if $\mathcal{E} = 2n+1$, $n = 0, 1, \dots$, 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

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

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

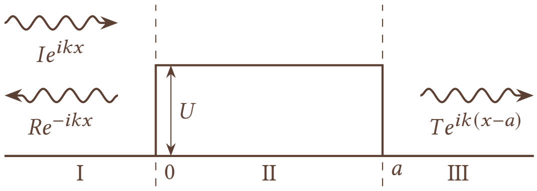
$$\psi(x) = \begin{cases} Ie^{ikx} + Re^{-ikx} & x < 0 \\ Te^{ikx} & x > a \end{cases}. \tag{30}$$

Scatter a wave of amplitude I. R is *reflexion coefficient*, T is *transmission coefficient*. For 1D solutions, probability current is constant since no ψ' term in TISE. Calculating current in both regions gives

$$|I|^2 = |R|^2 + |T|^2 . \tag{31}$$

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

4.1 Example: Square Barrier



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

We choose the solution between 0 and a carefully:

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

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

$$\begin{aligned} I + T &= A\cos\lambda a - B\tfrac{1}{\lambda}\sin\lambda a \\ ik(I - T) &= A\sin\lambda a + B\cos\lambda a \\ A &= R \\ B &= ikR \end{aligned} \tag{34}$$

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 $\mathbf{x}$”

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

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

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

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

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 comutation relation (CR) in quantum mechanics is

$$[x, p] = i\hbar. \tag{38}$$

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.
3. 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

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

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

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

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

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

Most famous is *Heisenberg's uncertainty principle* from applying this to (38),

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

5.3 Heisenberg and Ehrenfest

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

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

Ehrenfest's theorem Two specific examples are $\mathbf{x}$ and $\mathbf{p}$: we have

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

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

so “on average” the classical equations $\dot{\mathbf{x}} = \mathbf{p}/m$, $\dot{\mathbf{p}} = -\nabla V$ are satisfied by the system.

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 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

In 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 $x_i p_i$ 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:

$$[L^2, L_j] = 0, \tag{49}$$

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

$$p^2 = -\hbar^2\nabla^2 = -\hbar^2\frac{1}{r}\partial_r^2 r + \frac{L^2}{r^2}, \tag{50}$$

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 $L^2 Y = \hbar^2\ell(\ell+1)Y$, 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,

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

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. (See § 2.2)

7.3 Spherical Harmonics

Spherical harmonics $Y_\ell^m(\theta,\varphi)$ are simultaneous eigenfunctions of L^2 and L_3:

$$L^2 Y_\ell^m = \hbar^2\ell(\ell+1)Y_\ell^m, \quad L_3 Y_\ell^m = \hbar m Y_\ell^m. \tag{54}$$

Separating variables gives

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

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

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

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

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

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

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

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

For large y, equation looks like $R'' = -\nu^2 R$, so normalisable solution looks like $e^{-\nu y}$. 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 $R(y) = y^\ell e^{-\nu y}f(y)$, equation becomes

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

Changing variables to $\rho = 2\nu y$ gives

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

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

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

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