Quantum Mechanics II

lecture notes

Mr. Adrian Signer

Notes

Marc Maetz

FS 2013

Contents

Approximation methods for stationary problems

- standard QM problem:
  - given $|\psi(t_0)\rangle$
  - wanted

$$|\psi(t)\rangle = U(t, t_0)\,|\psi(t_0)\rangle$$
$$U = e^{-\frac{i}{\hbar}H(t-t_0)}$$

- for time independent H

$$U = e^{-\frac{i}{\hbar}H(t-t_0)} \tag{1.1}$$

find eigenvalue and eigenstates (diagonalize H)

but: most problems cannot be solved exactly → find approximate solution.

1.1 Time-independent perturbation theory, non-degenerate case

Assume:

$$H = H_0 + \lambda V \tag{1.2}$$

with H_0 the Hamiltonian that I can solve ("free" Hamiltonian) and the perturbation V "small" and λ a dimensionless bookkeeping par.

$$\lambda \to 0, \quad H \to H_0$$
$$\lambda \to 1, \quad \text{full } H$$

We know

$$\left|\psi_n^{(0)}\right\rangle, E_n^{(0)}$$

with

$$H_0\left|\psi_n^{(0)}\right\rangle = E_n^{(0)}\left|\psi_n^{(0)}\right\rangle$$

with

$$\left\langle\psi_n^{(0)}\middle|\psi_m^{(0)}\right\rangle = \delta_{mn}$$

(continuous spectrum also understood.)
We want $|\psi_n\rangle$ and E_n with

$$(H_0+\lambda V)|\psi_n\rangle = E_n|\psi_n\rangle$$

let

$$\begin{aligned} E_n &= E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \\ |\psi_n\rangle &= \left|\psi_n^{(0)}\right\rangle + \lambda\left|\psi_n^{(1)}\right\rangle + \lambda^2\left|\psi_n^{(2)}\right\rangle + \dots \end{aligned}$$

seems obvious, but assumption. (convergence?)

$$\begin{aligned} &\left(H_0 - E_n^{(0)}\right)\left|\psi_n^{(0)}\right\rangle + \lambda\left(\left(H_0 - E_n^{(0)}\right)\left|\psi_n^{(1)}\right\rangle\right) \\ &\quad + \lambda^2\left(\left(H_0 - E_n^{(0)}\right)\left|\psi_n^{(2)}\right\rangle + \left(V - E_n^{(1)}\right)\left|\psi_n^{(1)}\right\rangle - E_n^{(2)}\right) + \mathcal{O}\left(\lambda^3\right) = 0 \end{aligned}$$

with $\mathcal{O}(1)$ "step 0", $\mathcal{O}(\lambda)$ "step 1", $\mathcal{O}(\lambda^2)$ "step 2".

Step 0: nothing to do

Step 1 multiply by $\left\langle\psi_m^{(0)}\right|$

$$\begin{aligned} &\left\langle\psi_m^{(0)}\right| H_0 - E_n^{(0)}\left|\psi_m^{(0)}\right\rangle + \left\langle\psi_m^{(0)}\right| V - E_n^{(1)}\left|\psi_m^{(0)}\right\rangle = 0 \\ &= \left(E_m^{(0)} - E_n^{(0)}\right)\left\langle\psi_m^{(0)}\middle|\psi_n^{(1)}\right\rangle + \left\langle\psi_m^{(0)}\right| V\left|\psi_m^{(0)}\right\rangle - E_n^{(1)}\delta_{mn} = 0 \end{aligned}$$

to get $\left|\psi_n^{(1)}\right\rangle$

$$\begin{aligned} \left|\psi_n^{(1)}\right\rangle &= \sum_m \underbrace{\left\langle\psi_m^{(0)}\middle|\psi_n^{(1)}\right\rangle}\left|\psi_m^{(0)}\right\rangle \\ &= \sum_m \frac{\left\langle\psi_m^{(0)}\right| V\left|\psi_m^{(0)}\right\rangle}{E_n^{(0)} - E_m^{(0)}}\left|\psi_m^{(0)}\right\rangle + \left|\psi_n^{(0)}\right\rangle\left\langle\psi_n^{(0)}\middle|\psi_n^{(1)}\right\rangle \end{aligned}$$

from normalization

$$\langle \psi_n | \psi_n \rangle \overset{!}{=} 1 = \underbrace{\left\langle \psi_n^{(0)} \middle| \psi_n^{(0)} \right\rangle}_{1} + \lambda \underbrace{\left\langle \psi_n^{(0)} \middle| \psi_n^{(1)} \right\rangle}_{0} + \lambda \left\langle \psi_n^{(1)} \middle| \psi_n^{(0)} \right\rangle + \mathcal{O}\left(\lambda^2\right) \tag{1.3}$$

has to be small. If $E_n^{(0)} = E_m^{(0)}$?? degeneracy! $\rightarrow$ sec 1.2 if $E_n^{(0)} \simeq E_m^{(0)}$ quasi degenerate

step 2 take $\mathcal{O}(\lambda^2)$ terms $\left\langle \psi_k^{(0)} \right|$

$$\left(E_k^{(0)} - E_n^{(0)}\right) \left\langle \psi_k^{(0)} \middle| \psi_n^{(2)} \right\rangle + \left\langle \psi_k^{(0)} \middle| V \middle| \psi_k^{(0)} \right\rangle - E_n^{(1)} \left\langle \psi_k^{(0)} \middle| \psi_n^{(1)} \right\rangle = E_n^{(2)} \delta_{kn} \tag{1.4}$$

for $k = n$

$$\begin{aligned} E_n^{(2)} &= \left\langle \psi_n^{(0)} \middle| V \middle| \psi_n^{(0)} \right\rangle \\ &= \sum_{m \neq n} \frac{\left\langle \psi_n^{(0)} \middle| V \middle| \psi_n^{(0)} \right\rangle \left\langle \psi_m^{(0)} \middle| V \middle| \psi_m^{(0)} \right\rangle}{E_n^{(0)} - E_m^{(0)}} \\ &= \sum_{m \neq n} \frac{\| V_{nm}^2 \|}{E_n^{(0)} - E_m^{(0)}} \end{aligned} \tag{1.5}$$

Note $E_n^{(2)} < 0$ for ground state.
Next compute $\left| \psi_n^{(2)} \right\rangle$: initially fix normalization such that

$$\left\langle \psi_n^{(0)} \middle| \psi_n^{(i)} \right\rangle = \delta_{i0} \tag{1.6}$$

this is in conflict

$$\langle \psi_n | \psi_n \rangle = 1 \tag{1.7}$$

$\rightarrow$ sort out at the end.

$$\begin{aligned} \left| \psi_n^{(2)} \right\rangle &= \sum_{k \neq n} \left| \psi_k^{(0)} \right\rangle \left\langle \psi_k^{(0)} \middle| \psi_n^{(2)} \right\rangle + 0 \\ &= \sum_{k \neq n} \left| \psi_k^{(0)} \right\rangle \left(\frac{\left\langle \psi_k^{(0)} \middle| V \middle| \psi_k^{(0)} \right\rangle}{E_n^{(0)} - E_k^{(0)}} - \frac{E_n^{(1)} \left\langle \psi_k^{(0)} \middle| \psi_n^{(1)} \right\rangle}{E_n^{(0)} - E_k^{(0)}} \right) \end{aligned} \tag{1.8}$$

plug in $\left|\psi_n^{(1)}\right\rangle$ and sort out normalization

$$|\psi_n\rangle_N = \mathbb{Z}^{1/2}\,|\psi_n\rangle \tag{1.9}$$

fix such that

$$_N\langle\psi_n|\psi_n\rangle_M = 1 \tag{1.10}$$

$$\begin{aligned}
_N\langle\psi_n|\psi_n\rangle_N = 1 &\\
&= Z_n\,\langle\psi_n|\psi_n\rangle\\
&= Z_n\left(\left\langle\psi_n^{(0)}\right| + \lambda\left\langle\psi_n^{(1)}\right| + \lambda^2\left\langle\psi_n^{(2)}\right|\right)\\
&\quad\times\left(\left|\psi_n^{(0)}\right\rangle + \lambda\left|\psi_n^{(1)}\right\rangle + \dots\right)\\
&= E_n^{(2)}\delta_{kn}\\
&= Z_n\left(1 + \lambda^2\left\langle\psi_n^{(1)}\middle|\psi_n^{(1)}\right\rangle + \mathcal{O}\left(\lambda^3\right)\right)
\end{aligned}\tag{1.11}$$

$$Z_n^{1/2} = 1 - \frac{\lambda^2}{2}\left\langle\psi_n^{(1)}\middle|\psi_n^{(1)}\right\rangle\mathcal{O}\left(\lambda^3\right) \tag{1.12}$$

$$\Rightarrow\left|\psi_n^{(2)}\right\rangle$$

$$\begin{aligned}
&= \sum_{k\neq n}\sum_{m\neq n}\left|\psi_k^{(0)}\right\rangle\left[\frac{V_{km}-V_{mn}}{\left(E_n^{(0)}-E_k^{(0)}\right)\left(E_m^{(0)}-E_n^{(0)}\right)} - \frac{V_{kn}V_{nn}}{\left(E_n^{(0)}-E_n^{(0)}\right)}\right]\\
&\quad -\frac{1}{2}\sum_{k\neq n}\left|\psi_n^{(0)}\right\rangle\frac{\|V_{kn}^2\|}{\left(E_n^{(0)}-E_k^{(0)}\right)}
\end{aligned}\tag{1.13}$$

1.2 Time-independent perturbation theory: degenerate case

Assume $E_n^{(0)}$ is α-fold degenerate i.e.

$$H_0\left|\psi_{n_i}^{(0)}\right\rangle = E_n^{(0)}\left|\psi_n^{(0)}\right\rangle,\quad 1\le i\le\alpha \tag{1.14}$$

fix

$$\left\langle\psi_{n_i}^{(0)}\middle|\psi_{n_j}^{(0)}\right\rangle = \delta_{ij} \tag{1.15}$$

Any linear combination

$$\left|\chi_n^{(0)}\right\rangle = \sum_{i=1}^{\alpha} c_{n_i}\left|\psi_{n_i}^{(0)}\right\rangle \tag{1.16}$$

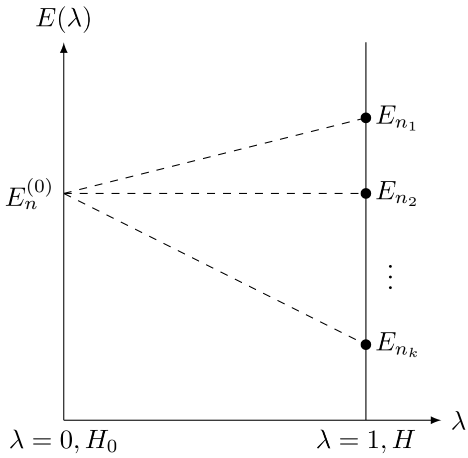

Figure 1.1:

is an eigenstate of H_0 with evaluation $E_n^{(0)}$ Typically V "lifts" degeneracy at least partially since often

$$[H_0, V] \neq 0 \tag{1.17}$$

Pick one of the evals E_{n_k} with

$$H\left|\psi_{n_k}\right\rangle = E_{n_k}\left|\psi_{n_k}\right\rangle \tag{1.18}$$

for $\lambda \to 0$: $E_{n_k} \to E_n^{(0)}$ and

$$\begin{aligned}\left|\psi_{n_k}\right\rangle &\to \left|\chi_{n_k}(0)\right\rangle \\ &= \sum_{i=1}^{\alpha} \underbrace{c_{n_k i}\left|\psi_{n_i}^{(0)}\right\rangle}_{\substack{\text{some lin}\\ \text{comb}}}\end{aligned} \tag{1.19}$$

have to find "good" linear combination, i.e. coeff $c_{n_k i}$. Main idea as before:

$$\left|\psi_{n_k}\right\rangle = \left|\chi_{n_k}^{(0)}\right\rangle + \lambda\left|\psi_{n_k}^{(1)}\right\rangle \tag{1.20}$$

$$0 = \left(H_0 - E_n^{(0)}\right)\left|\psi_{n_k}^{(1)}\right\rangle + \left(V - E_{n_k}^{(1)}\right)\left|\chi_{n_k}^{(1)}\right\rangle \tag{1.21}$$

with

$$\left|\psi_{n_k}^{(1)}\right\rangle = \sum_{\ell=1}^{\dim(H_0)} a_{n_\ell}\left|\psi_\ell^{(0)}\right\rangle \tag{1.22}$$

and

$$\sum_{i=1}^{\alpha} c_{n_k i} \left| \psi_{n_i}^{(0)} \right\rangle \tag{1.23}$$

multiply by $\left\langle \psi_{n_j}^{(0)} \right|$.

$$\sum_{\ell=1}^{\dim H_0} \underbrace{\left(E_\ell^{(0)} - E_n^{(0)} \right)}_{=0 \text{ for } n=\ell} a_{n\ell} \underbrace{\left\langle \psi_{n_j}^{(0)} \middle| \psi_\ell^{(0)} \right\rangle}_{=0 \text{ for } n\neq\ell} + \sum_{i=1}^{\alpha} c_{n_k i} \left(\left\langle \psi_{n_j}^{(0)} \right| V \left| \psi_{n_j}^{(0)} \right\rangle \right. \\ \left. - E_{n_k}^{(1)} \underbrace{\left\langle \psi_{n_j}^{(0)} \middle| \psi_{n_i}^{(0)} \right\rangle}_{V_{ji}} - E_{n_k}^{(1)} \underbrace{\left\langle \psi_{n_j}^{(0)} \middle| \psi_{n_i}^{(0)} \right\rangle}_{\delta_{ij}} \right) \tag{1.24}$$

→ solve

$$\det \begin{pmatrix} V_{11} - E_{n_k}^{(1)} & V_{12} & \dots & V_{1\alpha} \\ V_{21} & V_{22} - E_{n_k}^{(1)} & \dots & \vdots \\ \vdots & \vdots & \ddots & \vdots \\ V_{\alpha 1} & \dots & \dots & V_{\alpha\alpha} - E_{n_k}^{(1)} \end{pmatrix} = 0 \tag{1.25}$$

→ eq. of order $\propto$ in $E_{n_k}^{(1)}$
→ α solutions

1.2.1 easy way out (sometimes)

if $V_{ij} = 0$ for $i \neq j$ problem already solved
→ α solutions are

$$E_{n_i}^{(1)} = \left\langle \psi_i^{(0)} \right| V \left| \psi_i^{(0)} \right\rangle \tag{1.26}$$

Note: if $\exists$ operator A with

$$[A, V] = 0 \tag{1.27a}$$

and

$$A \left| \psi_{n_i}^{(0)} \right\rangle = a_{n_i} \left| \psi_{n_i}^{(0)} \right\rangle, \tag{1.27b}$$

with

$$a_{n_i} \neq a_{n_k}, \quad \text{for } k \neq i \tag{1.27c}$$

then these $\left|\psi_{n_i}^{(0)}\right\rangle$ are "good" eigenstates

Proof:

$$\begin{aligned}\left\langle\psi_{n_i}^{(0)}\right| [A,V] \left|\psi_{n_i}^{(0)}\right\rangle &= 0 \\ &= \underbrace{(a_{n_i} - a_{n_k})}_{\neq 0} \underbrace{\left\langle\psi_{n_i}^{(0)}\right| V \left|\psi_{n_i}^{(0)}\right\rangle}_{V_{ik}}\end{aligned} \tag{1.28a}$$

$$\Rightarrow V_{ik} = 0 \tag{1.28b}$$

1.3 The variational principle

Useful to get good estimate of ground-state energy E_0 of complicated systems. Claim

$$E_0 \leq \frac{\langle\psi| H |\psi\rangle}{\langle\psi|\psi\rangle} = \langle\psi| H |\psi\rangle \tag{1.29}$$

if $|\psi\rangle$ normalized.

Proof: Let

$$|\psi\rangle = \sum c_n |\psi_n\rangle , \tag{1.30a}$$

with

$$H |\psi_n\rangle = E_n |\psi_n\rangle \tag{1.30b}$$

and

$$\langle\psi|\psi\rangle = 1 \tag{1.30c}$$

$$\Rightarrow \sum \|c_n\|^2 = 1 \tag{1.30d}$$

then

$$\begin{aligned}\langle\psi| H |\psi\rangle &= \sum_{m,n} c_m^* c_n \langle\psi_m| H |\psi_m\rangle = \sum_{m,n} c_m^* c_n E_n \underbrace{\langle\psi_m|\psi_n\rangle}_{\delta_{mn}} \\ &= \sum_n \|c_n\|^2 E_n \geq E_0 \sum_n \|c_n\|^2 = E_0\end{aligned} \tag{1.30e}$$

Example 1.3.1 (Harmonic oscillator):

$$H = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\frac{m}{2}\omega^2 x^2 \tag{1.31}$$

(of course we know $E_0 = \frac{\hbar}{2}\omega$). Let

$$\psi(x) = Ae^{-bx^2} \tag{1.32a}$$

since

$$\begin{aligned}\langle\psi|\,\psi\rangle \stackrel{!}{=} 1 &= \int \mathrm{d}x\, \|A\|^2 e^{-2bx^2} \\ &= \|A\|^2\sqrt{\frac{\pi}{2b}}\end{aligned} \tag{1.32b}$$

compute

$$\begin{aligned}\langle\psi|\, H\,|\psi\rangle &= \|A\|^2 \int \mathrm{d}x\, e^{-bx^2}\left(-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\frac{m}{2}\omega^2x^2\right)e^{-bx^2} \\ &= \dots \\ &= \frac{\hbar^2 b}{2m} + \frac{m\omega^2}{8b} \\ &= \langle\psi|\, H\,|\psi\rangle \\ &\geq E_0\end{aligned} \tag{1.32c}$$

Minimize with respect to b

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}b}\langle\psi|\, H\,|\psi\rangle &= \frac{\hbar^2}{2m} - \frac{m\omega^2}{8b^2} \\ &= 0\end{aligned} \tag{1.33a}$$

$$b_{\min} = \frac{m\omega}{2\hbar} \tag{1.33b}$$

$$\begin{aligned}E_0 &\leq \langle\psi|\, H\,|\psi\rangle_{\min} \\ &= \frac{\hbar\omega}{2}\end{aligned} \tag{1.33c}$$

in this case we get E_0 exactly is a coincidence, since Ansatz=true wave function.

1.4 WKB approximation, semiclassical approximation

WKB for Wentzel, Kramers, Brillouin (see QMI Ch. 8.3.) useful for 1-dim problems with "smooth" popential. Schrödinger:

$$\left(-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}V(x)\right)\psi(x) = E\psi(x) \tag{1.34a}$$

if

$$V(x) \equiv V_0 \text{ const.} \tag{1.34b}$$

$$\psi(x) = e^{\pm\frac{i}{\hbar}\sqrt{2m(E-V_0)}x} \tag{1.34c}$$

if $V(x)$ is slowly varying. Ansatz

$$\psi(x) = e^{\frac{i}{\hbar}S(x)} \tag{1.34d}$$

Ansatz into Schrödinger:

$$\frac{-i\hbar}{2m}S'' + \frac{1}{2m}\left(S'\right)^2 + V(x) - E = 0 \tag{1.34e}$$

equivalent to but more complicated than Schrödinger. Note for

$$V(x) \equiv V_0$$

$$S = \pm\sqrt{2m\left(E - V_0\right)} \cdot x$$

and

$$S'' = 0$$

first term $\sim \hbar$ vanishes for

$$V(x) \equiv V_0, \quad (\text{classical limit})\,,$$

Let

$$S(x) = S_0(x) + \hbar S_1(x) + \mathcal{O}(\hbar^2) \tag{1.35a}$$

plug in into differential equation for S

$$\frac{1}{2m}\left(S_0'\right)^2 + V(x) - E = 0 \tag{1.35b}$$

$$\begin{aligned}\Rightarrow S_0' &= \pm\sqrt{2m\left(E - V(x)\right)} \\ &\equiv \pm p(x)\end{aligned} \tag{1.35c}$$

$$S_0'S_1' - \frac{1}{2}S_0'' = 0 \tag{1.35d}$$

$$\Rightarrow S_1' = \frac{i}{2}\frac{S_0''}{S_0'} = \frac{i}{2}\frac{p'(x)}{p(x)} \tag{1.35e}$$

solve these differential equation

$$S_0 = \pm \int^x \mathrm{d}x' \, p(x') \tag{1.35f}$$

$$S_1 = \frac{i}{2} \ln p(x) \tag{1.35g}$$

$$\begin{aligned} \Rightarrow \psi(x) &= A e^{\frac{i}{\hbar}(S_0 + \hbar_1)} \\ &= \frac{A_+}{\sqrt{p(x)}} e^{\frac{i}{\hbar} \int \mathrm{d}x' \, p(x')} + \frac{A_-}{\sqrt{p(x)}} e^{-\frac{i}{\hbar} \int \mathrm{d}x' \, p(x')} \end{aligned} \tag{1.35h}$$

Chapter 2

The hydrogen atom

2.1 Basics

Two body problem proton (1)-electron (2)

$$H = -\frac{\hbar^2}{2m_2}\boldsymbol{\nabla}_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V\left(\mathbf{r}_1 - \mathbf{r}_2\right) \tag{2.1}$$

new variables

$$R = \frac{m_2 r_1 + m_2 r_2}{m_1 + m_2} \tag{2.2}$$

$$r = r_1 - r_2 \tag{2.3}$$

$$M = m_1 + m_2 \tag{2.4}$$

$$m = \frac{m_1 m_2}{m_1 + m_2} \tag{2.5}$$

$$H = -\frac{\hbar^2}{2M} \tag{2.6}$$

2.2 Spin-orbit term

naive "derivation"

(1) Electron with spin → magnetic dipole moment

$$\boldsymbol{\mu} = \frac{e}{m}\frac{g}{2}\mathbf{s}\,, \tag{2.7}$$

$$\mu = \frac{e}{T}\pi r^2\,, \quad s = \frac{2\pi}{T}mr^2\,, \quad g \simeq \text{ (from Dirac)} \tag{2.8}$$

(2) Electron feeds magnetic field due to the proton

$$\mathbf{E} \sim \frac{e}{r3}\mathbf{r} \tag{2.9}$$

$$\begin{aligned} \rightarrow \mathbf{B} &= -\frac{1}{c^2}\boldsymbol{\nabla} \times \mathbf{E} \\ &= -\frac{1}{mc^2r^3}\mathbf{p} \times \mathbf{r} \\ &= \frac{-\mathbf{L}}{mc^2r^3} \end{aligned} \tag{2.10}$$

wrong by factor 2 (Thomas precession)

...correct result

$$H_{\mathrm{SO}} = \frac{Ze^2}{2mc^2}\frac{1}{r^3}\mathbf{L}\cdot\mathbf{S}, \quad (\sim -\boldsymbol{\mu}\cdot\mathbf{B}) \tag{2.11}$$

To describe spin

$$\begin{aligned} \left| n, \ell, \left(s = \frac{1}{2}, m_s\right)\right\rangle &= \psi_{n\ell m_\ell m_s} \\ &= \psi_{n\ell m_\ell}(r, \theta\varphi)\, \chi_{m_s} \end{aligned} \tag{2.12a}$$

with χ_{m_s} spin-orbit

$$\begin{pmatrix}1\\0\end{pmatrix}\begin{pmatrix}0\\1\end{pmatrix} \tag{2.12b}$$

Note H_{SO} "mixes" states with same ℓ, but different m_ℓ, m'_ℓ
$\rightarrow$ use degenerate perturbation theory with $2\cdot(2\ell+1)\times\underbrace{2}_{\text{spin}}\underbrace{(2\ell+1)}_{m_\ell}$ matrix

$$\langle n, \ell, m'_\ell, m'_s|\, H_{\mathrm{SO}}\, |n, \ell, m'_\ell, m'_s\rangle \rightarrow \text{diagonalize} \tag{2.13}$$

recall degenerate perturbation theory $\rightarrow$ find "good" linear combination that diagonalize this matrix by looking for symmetry use total angular momentum

$$J \equiv L + S \tag{2.14}$$

for $\ell = 0 \quad j = \frac{1}{2}$, for $\ell \neq 0 \quad j = \ell \pm \frac{1}{2}$. Use states

$$|n, \ell, j, m_j\rangle \tag{2.15}$$

$$|n,\ell,j,m_j\rangle = \sum_{m_\ell,m_s} |n,\ell,m_\ell,m_s\rangle \underbrace{\langle n,\ell,m_\ell,m_s|n,\ell,j,m_j\rangle}_{\text{Clebsch-Gordan}} \tag{2.16}$$

use

$$J^2 = L^2 + 2L\cdot S + S^2 \tag{2.17a}$$

$$L\cdot S = \frac{1}{2}\left(J^2 - L^2 - S^2\right) \tag{2.17b}$$

$|n,\ell,j,m_j\rangle$ are eigenstates of

$$H_0, L^2, S^2, J^2, J_z \tag{2.18}$$

with eigenvalues

$$E_n, \hbar^2\ell\left(\ell+1\right), \hbar^2\frac{3}{4}, \hbar^2 j\left(j+1\right), \hbar m_j \tag{2.19}$$

$$\Delta E_{\text{SO}} = \langle n,\ell,j,m_j|\, H_{\text{SO}}\, |n,\ell,j,m_j\rangle \tag{2.20}$$

for $\ell = 0$

$$\Delta E_{\text{SO}} = 0 \tag{2.21a}$$

for $\ell \neq 0$

$$\begin{aligned}\Delta E_{\text{SO}} &= \frac{Ze^2}{2m^2c^2}\langle n,\ell,j,m_j|\,\frac{1}{r^3}\frac{1}{2}\left(J^2-L^2-S^2\right)|n,\ell,j,m_j\rangle \\ &= \frac{Ze^2}{2m^2c^2}\left\langle\frac{1}{r^3}\right\rangle\frac{\hbar^2}{2}\left(j\left(j+1\right)-\ell\left(\ell+1\right)-\frac{3}{4}\right) \\ &= -E_n\frac{\left(Z\alpha\right)^2}{2n\left(\ell+\frac{1}{2}\right)}\begin{cases}\frac{1}{\ell+1} & j=\ell+\frac{1}{2}\\ -\frac{1}{\ell} & j=\ell-\frac{1}{2}\end{cases}\end{aligned} \tag{2.21b}$$

2.3 Darwin term

Sloppy consideration electron position fluctuates by $\delta r \simeq \lambda_c \simeq \frac{\hbar}{mc}$ electron feels average potential

$$\langle V\left(r+\delta r\right)\rangle = \langle V(r)\rangle + \underbrace{\frac{1}{2}\langle\boldsymbol{\delta}\rangle\, r\cdot\boldsymbol{\nabla}\boldsymbol{\delta}r\cdot\nabla V} \tag{2.22}$$

correct result is

$$\begin{aligned} H_D &= \frac{\hbar^2}{8m^2c^2}\nabla^2 V \\ &= \frac{\pi\hbar^2 Ze^2}{2m^2c^2}\delta(r) \end{aligned} \tag{2.23}$$

only for $\ell = 0$!

$$\begin{aligned} \Delta E_D &= \langle n, \ell, j, m_j | \, H_D \, | n, \ell, j, m_j \rangle \\ &= \frac{\pi\hbar^2 Ze^2}{2m^2c^2} \|\psi_{n\ell}(0)\|^2 \\ &= -E_n \frac{(Z\alpha)^2}{n}\delta_{\ell 0} \end{aligned} \tag{2.24}$$