Ph125b Notes

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Contents

Results

1: Logistics

- Gradescope
- Piazza

1.1. Notation

- Typesetter Notation: <u>Underlining</u> is typesetting for bold, so $\underline{x} = \boldsymbol{x} = \vec{x}$

2: WKB Method

The goal of the Wentzel-Krumers-Brillouin Method is to estimate the spectrum of a Hamiltonian by maaking use of the wave-nature of the Schrodinger Equation in correspodnence to the classical turning points. We begin by labelling the energy eigenstates by $|0\rangle, |1\rangle, |2\rangle, \ldots$ and the respective eigenvalues, $E_0, E_1, E_2, \ldots$

Consider now E_n with classical turning points (x_1, x_2) within a single interval. E_n corresponds to the $(n+1)$-th state, or the n-th excited state. Between the classical turning points, the wavefunction will be primarily oscillatory, as can be seen by the Schrodinger Equation. In particular, there will be roughly $n+1$ half-waves between the two turning points. Stating this more formally, let $\Delta\varphi_n$ be the total phase change of the the wave function between the turning points for $|n\rangle$. We have:

$$\Delta\varphi_n \approx \left(n + \frac{1}{2}\right)\pi \tag{2.0.1}$$

or more rigorously,

$$n\pi < \Delta\varphi_n \leq (n+1)\pi \tag{2.0.2}$$

where equality would if, for example, we had an infinite square well potential. Here, we'll just assume the previous approximate value.

Now recognize that for a region of constant $V < E_n$, we must have:

$$\psi(x) = A \sin P(x - x_0) \tag{2.0.3}$$

where A, x_0 are constants and

$$P = \sqrt{2m(E - V)} \tag{2.0.4}$$

Without loss of generality,

$$\varphi(x) = p(x - x_0) \tag{2.0.5}$$

in the region of constant V. But we may generalize this for non-constant V with:

$$\mathrm{d}\varphi(x) = p\mathrm{d}x = \sqrt{2m(E - V)}\mathrm{d}x \tag{2.0.6}$$

And we find that we must have:

$$\Delta\varphi = \int_{x_1}^{x_2} \frac{\mathrm{d}\varphi}{\mathrm{d}x}\mathrm{d}x = \int_{x_1}^{x_2} \sqrt{2m(E - V)}\mathrm{d}x \tag{2.0.7}$$

but from the previous approximation, we must have:

$$\left(n + \frac{1}{2}\right)\pi \approx \int_{x_1}^{x_2} \sqrt{2m(E - V)}\mathrm{d}x \tag{2.0.8}$$

This gives us a reasonable approximation for the energy levels for any given potential (which also provides x_1, x_2).

> **Example 2.0:1 (Infinite Square Well)**
>
> We have:
> $$x_1 = 0 \quad ; \quad x_2 = \Delta \quad ; \quad V = 0 \tag{2.0.9}$$
>
> Therefore:
> $$\int_0^\Delta \sqrt{2mE}\mathrm{d}x = \sqrt{2mE}\Delta \tag{2.0.10}$$
>
> $$\sqrt{2mE}\Delta \approx \left(n + \frac{1}{2}\right)\pi \tag{2.0.11}$$
>
> $$E_n = \frac{\left(n + \frac{1}{2}\right)^2 \pi^2}{2m\Delta^2} \tag{2.0.12}$$
>
> Giving the exact answer. We could have also solved this from the fact that the boundary conditions inherently specify the exact change in phase.

> **Example 2.0:2 (1D Harmonic Oscillator)**
>
> We again have:
> $$x_1 = -x_2 = \sqrt{2\frac{E}{k}} \quad ; \quad V(x) = \frac{1}{2}kx^2 \tag{2.0.13}$$
>
> Now:
> $$2\sqrt{mk}\int_0^{x_0} \sqrt{x_0^2 - x^2}\mathrm{d}x \tag{2.0.14}$$
>
> $$= \pi\sqrt{mk}\frac{x_0^2}{2} = \pi\frac{E}{\omega_0} \quad ; \quad \omega_0 = \sqrt{\frac{k}{m}} \tag{2.0.15}$$
>
> $$\approx \left(n + \frac{1}{2}\right)\pi \Rightarrow E_n = \left(n + \frac{1}{2}\right)\omega_0 \tag{2.0.16}$$
>
> which is once again an exact result.

3: Variational Method

3.1. The Idea

The idea is that when we have some Schrodinger Equation with a given potential, we resort to a variational method to determine the ground energy. The process is as follows:

- Make an educated guess for a solution to the Schrodinger Equation.
- Parameterize it.
- Use variational calculus to minimize $\langle \psi | H | \psi \rangle$.
- Obtain an upper bound on the ground state energy.

Let E_0 be the ground state energy. Note that for any wavefunction $\psi \in \mathcal{H}$, that we must have:

$$\frac{\langle \psi | H | \psi \rangle}{\langle \psi \,|\, \psi \rangle} \geq E_0 \tag{3.1.1}$$

This suggests using some set of ψ parameterized by some variable, call it Θ. We can then vary Θ and minimize the quantity above using variational calculus:

$$\frac{\delta \left\{ \frac{\langle \psi[\Theta] | H | \psi[\Theta] \rangle}{\langle \psi[\Theta] \,|\, \psi[\Theta] \rangle} \right\}}{\delta \{\Theta\}} = 0 \tag{3.1.2}$$

3.2. Examples

> **Example 3.2:3 (The Helium Atom)**
>
> Let $\boldsymbol{R} = \boldsymbol{r}_1 - \boldsymbol{r}_2$
>
> $$H = \frac{\widehat{\boldsymbol{P}}_1^2}{2m} + \frac{\widehat{\boldsymbol{P}}_2^2}{2m} - \frac{2\alpha}{|\boldsymbol{r}_1|} - \frac{2\alpha}{|\boldsymbol{r}_2|} + \frac{\alpha}{|\boldsymbol{R}|} \tag{3.2.1}$$
>
> Where $m = m_e$ and neglecting the motion of the nucleus.
>
> **Note that the difficulty of the problem comes from the interaction term, which prevents it from becoming just the hydrogen atom, twice.**

Guess:

$$\psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \frac{Z^3}{\pi} a_0^3 \exp\left(-\frac{Z}{a_0}(\boldsymbol{r}_1 + \boldsymbol{r}_2) \right) \tag{3.2.2}$$

Where

$$Z = 2 \quad ; \quad a_0 = \frac{1}{m\alpha} \tag{3.2.3}$$

> **Remark 3.2:4**
>
> Note there is no reason to expect that the interaction term to be "small." It is roughly of the same order as the two other Coulomb potentials in the Hamiltonian. When we get to Pertubation theory, we'll see that we can add "small" corrections, but this is where the Variational method shines.

We will be choosing Z as our variational parameter. We note that $\psi[\Theta]$ is already normalized. We start by taking the expectation value of H:

$$\left\langle \psi \left| \frac{\widehat{P}_1^2}{2m} \right| \psi \right\rangle = \int d^3(\boldsymbol{x}_1) \left(\frac{Z^3}{\pi a_0^3} e^{-\frac{Z}{a_0} r_1} \right) \frac{\widehat{P}_1^2}{2m} \left(\frac{Z^3}{\pi a_0^3} e^{-\frac{Z}{a_0} r_1} \right) \tag{3.2.4}$$

$$= Z^2 \times (\text{K.E. of the H atom ground state.}) \tag{3.2.5}$$

$$= \frac{Z^2}{2} m\alpha^2 \tag{3.2.6}$$

$$\Rightarrow \langle \psi | \frac{\widehat{P}_1^2 + \widehat{P}_2^2}{2m} | \psi \rangle = Z^2 m\alpha^2 \tag{3.2.7}$$

Likewise we can do something similar for the Coulomb term:

$$\left\langle \psi \left| -2\frac{\alpha}{r_1} \right| \psi \right\rangle = 2Z(\text{P.E. of the H atom ground state.}) \tag{3.2.8}$$

$$= -2Zm\alpha^2 = -2\alpha \langle \frac{1}{r_1} \rangle \tag{3.2.9}$$

So far we have:

$$\Rightarrow \left\langle \psi \left| \frac{\widehat{P}_1^2 + \widehat{P}_2^2}{2m} - 2\alpha \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \right| \psi \right\rangle = \frac{1}{2} m\alpha (2Z^2 - 8Z) \tag{3.2.10}$$

Now we just need the last piece:

$$\left\langle \psi \left| \frac{\alpha}{R} \right| \psi \right\rangle = \alpha \iint d^2(\boldsymbol{r}_1) d^3(\boldsymbol{r}_2) \tag{3.2.11}$$

Let's now take a moment to digress to some handy integrals we'll need in the future:

> **Theorem 3.2:5**
>
> If $u > 0$ and $v > 0$ (one of which may be 0 but not both).
>
> $$I(u, v; \boldsymbol{x}', \boldsymbol{x}'') := \int d^3(\boldsymbol{y}) \frac{\exp(-u\,|\boldsymbol{y} - \boldsymbol{x}'\,| - v\,|\boldsymbol{y} - \boldsymbol{x}''\,|)}{|\boldsymbol{y} - \boldsymbol{x}'|\,|\boldsymbol{y} - \boldsymbol{x}''|} \tag{3.2.12}$$
>
> $$= \frac{4\pi \left(e^{-v\Delta} - e^{-u\Delta} \right)}{\Delta(u^2 - v^2)} \tag{3.2.13}$$
>
> Where
>
> $$\Delta = |\boldsymbol{x}' - \boldsymbol{x}''| \tag{3.2.14}$$

> **Theorem 3.2:6**
>
> If $u > 0, v > 0, w > 0$ (only one of which may be 0), then
>
> $$J(u, v, w) := \int \mathrm{d}^3(\boldsymbol{x})\mathrm{d}^3(\boldsymbol{y})\frac{\exp(-u\,|\,\boldsymbol{x}\,|-v\,|\,\boldsymbol{y}\,|-w\,|\,\boldsymbol{x}-\boldsymbol{y}\,|)}{|\boldsymbol{x}|\,|\boldsymbol{y}|\,|\boldsymbol{x}-\boldsymbol{y}|} \tag{3.2.15}$$
>
> $$= \frac{(4\pi)^2}{(u+v)(v+w)(w+u)} \tag{3.2.16}$$

Sketch of Proof 3.2:6:
- Let $\boldsymbol{z} = \boldsymbol{y} - \boldsymbol{x}$ and $|\boldsymbol{z}| = r$.
- Move to $\mathrm{d}^3(\boldsymbol{z})$
- Apply spherical coordinates to the integral.
- Pick 3-axis along $\boldsymbol{x} - \boldsymbol{y}$ direction.
- Integrate over the angles.
- Apply trig identity (?).
- Integrate over radius.

$\square$

Lecture ended here. Results will be shown next time.

$$\left\langle \psi \,\middle|\, \frac{\alpha}{\boldsymbol{R}} \,\middle|\, \psi \right\rangle = \alpha \iint_\infty \mathrm{d}^3(\boldsymbol{x}_1)\mathrm{d}^3(\boldsymbol{x}_2)\left(\frac{Z^3}{\pi a_0^2}\right)^2 \frac{\exp\left(-\frac{2Z}{a_0}\right)(\boldsymbol{r}_1 + \boldsymbol{r}_2)}{\|\boldsymbol{x}_1 - \boldsymbol{x}_2\|} \tag{3.2.17}$$

$$= \alpha \left(\frac{Z^3}{\pi a_0^2}\right)^2 \iint_\infty \mathrm{d}^3(\boldsymbol{x})\mathrm{d}^3(\boldsymbol{y})\frac{\exp\left(-2\frac{Z}{a_0}(\boldsymbol{x} + \boldsymbol{y})\right)}{\|\boldsymbol{x} - \boldsymbol{y}\|} \tag{3.2.18}$$

Can be put into the form of

$$J(u, v, w) := \int_\infty \mathrm{d}^3(\boldsymbol{x}) \int_\infty \mathrm{d}^3(\boldsymbol{y})\frac{\exp(-u\|\boldsymbol{x}\| - v\|\boldsymbol{y}\| - w\|\boldsymbol{x} - \boldsymbol{y}\|)}{\|\boldsymbol{x}\|\|\boldsymbol{y}\|\|\boldsymbol{x} - \boldsymbol{y}\|} \tag{3.2.19}$$

Where this is now integrable by **Theorem 2**. We then obtain:

$$= \alpha \left(\frac{Z^3}{\pi a_0^2}\right)^2 \partial_u \partial_v J(u, v, 0) \tag{3.2.20}$$

$$= \frac{1}{2}m\alpha^2 \frac{5}{4}Z \tag{3.2.21}$$

$$\langle \psi \,|\, H \,|\, \psi \rangle = \frac{1}{2}m\alpha^2 \left(2z^2 - 8z + \frac{5}{4}z\right) = \frac{1}{2}m\alpha^2 \left(2z^2 - \frac{27}{4}z\right) \tag{3.2.22}$$

Minimality implies

$$0 = 4Z - \frac{27}{4} \Rightarrow z = \frac{27}{16} \tag{3.2.23}$$

$$-\frac{1}{2}m\alpha^2 \left(2\left(\frac{27}{16}\right)^2\right) \approx -77.0 \ eV \tag{3.2.24}$$

Experiment gives:

$$-78.60 \ e\text{V}, \quad +2\% \ \text{of our guess.} \tag{3.2.25}$$

The fact that the minimum value for $Z = \frac{27}{16}$ also tells us something else. That the "effective charge" of the nucleus is reduced by the screening of the electrons.

Theorem 3.2:7 (Variational Theorem)

Let $\psi \in \mathcal{H} \mid 0 < \langle \psi \mid \psi \rangle < \infty$. Definite the functional:

$$E[\psi] := \frac{\langle \psi \mid H \mid \psi \rangle}{\langle \psi \mid \psi \rangle} \tag{3.2.26}$$

and H a linear operator with a discrete spectrum. Then any $\psi \mid$ variation is stationary, that is, $\delta(E[\psi]) = 0$ is an eigenvector of H with eigenvalue $E(\psi)$ and vice-versa.

Proof 3.2:8:

$$E[\psi]\langle \psi \mid \psi \rangle = \langle \psi \mid H \mid \psi \rangle \tag{3.2.27}$$

$$\delta(E[\psi]\langle \psi \mid \psi \rangle) = \delta\langle \psi \mid H \mid \psi \rangle \tag{3.2.28}$$

$$(\delta E[\psi])\langle \psi \mid \psi \rangle + E[\psi]\langle \delta\psi \mid \psi \rangle + E[\psi]\langle \psi \mid \delta\psi \rangle = \langle \delta\psi \mid H \mid \psi \rangle + \langle \psi \mid H \mid \delta\psi \rangle \tag{3.2.29}$$

Where $\delta H = 0$ since it's an operator independent of our parameter.

$$\delta E[\psi]\langle \psi \mid \psi \rangle = \langle \delta\psi \mid H - E \mid \psi \rangle + \langle \psi \mid H - E \mid \delta\psi \rangle \tag{3.2.30}$$

If $(H - E)|\psi\rangle = 0$, then $\delta E = 0$, i.e. if ψ is an eigenstate then it is then the $E[\psi]$ is stationary.

Suppose now that $\delta E = 0$. Then:

$$\langle \delta\psi \mid H - E \mid \psi \rangle + \langle \psi \mid H - E \mid \delta\psi \rangle = 0 \tag{3.2.31}$$

But ψ is complex. And so in particular variation is independent over both the real parts and the imaginary parts. And if $\delta E = 0$,

$$\langle \delta(i\psi) \mid H - E \mid \psi \rangle + \langle \psi \mid H - E \mid \delta(i\psi) \rangle = 0 \tag{3.2.32}$$

$$-i\langle \delta\psi \mid H - E \mid \psi \rangle + i\langle \psi \mid H - E \mid \delta\psi \rangle = 0 \tag{3.2.33}$$

Adding the previous equation,

$$\langle \delta\psi \mid H - E \mid \psi \rangle = 0, \forall \delta\psi \tag{3.2.34}$$

$$\Rightarrow H|\psi\rangle = E|\psi\rangle \tag{3.2.35}$$

$\square$

3.3. Rayleigh-Ritz Variational Method

Imagine choosing a set of trial, orthonormal wave functions. With the helium method, we chose parameterized wave functions. Now, we'll take this independent set and form linear combinations of them. Let us label them $|n\rangle$ for $n \in \mathbb{N} < N$.

$$|\psi\rangle = \sum_n a_n |n\rangle \tag{3.3.1}$$

The a_n are $N + 1$ complex parameters to be varied. Requiring $\langle \psi, \psi \rangle = 1$ we constrain

$$\sum_n \|a_n\|^2 = 1 \tag{3.3.2}$$

We want to find $\{a_n\}$ such that $\delta\langle\psi\,|\,H\,|\,\psi\rangle = 0$. Then

$$0 = \delta\left(\sum_{m,n}\langle\psi\,|\,m\rangle\langle m\,|\,H\,|\,n\rangle\langle n\,|\,\psi\rangle\right) \tag{3.3.3}$$

subject to

$$0 = \delta(1) = \delta\left(\sum_n\|a_n\|^2\right) = \psi\left(\sum_{m,n}a_m^*a_n\delta_{m,n}\right) \tag{3.3.4}$$

Which we include with the Lagrange multiplier:

$$\psi\left(\sum_{m,n}a_m^*a_n\langle m\,|\,H\,|\,n\rangle\right) = \delta\left(\lambda\sum_{m,n}a_m^*a_n\delta_{m,n}\right) \tag{3.3.5}$$

$$0 = \sum_{m,n}(\delta a_m^*a_n(\langle m\,|\,H\,|\,n\rangle) - \lambda\delta_{m,n} + a_m^*(\delta a_n)(\langle m\,|\,H\,|\,n\rangle) - \lambda\delta_{m,n} \tag{3.3.6}$$

$$\Rightarrow \sum_n a_n[\langle m\,|\,H\,|\,n\rangle - \lambda\delta_{mn}] = 0 \tag{3.3.7}$$

or

$$\left\langle m\,\middle|\,(H-\lambda)\sum_n a_n\,\middle|\,n\right\rangle \quad \forall m \Rightarrow \{a_m, \lambda\} \tag{3.3.8}$$

In this reduced basis in the original subspace of $\{a_m\}$

$$\sum_n a_n^{(i)}|n\rangle \tag{3.3.9}$$

are N linearly independent eigenvectors of H with eigenvectors $E^{(i)} = \lambda^{(i)}$ Where $a^{n^{(i)}}$ is

If picked well, the first few $E^{(i)}$ may be good estimate for first few energies.

4: Stationary State Approximation

This approximation is also called Time-Independent Pertubation Theory. We start by looking for a series expansion that converges for "small pertubations" on a Hamiltonian we've solved.

Consider the Hamiltonian:

$$H = H_0 + V \tag{4.0.10}$$

where H_0 is a solved Hamiltonian, that is,

$$H_0|n\rangle = \varepsilon_n|n\rangle \tag{4.0.11}$$

But we're now interested in solving the same problem for H. If V is relatively small compared to the potential of H_0, call it V_0, then we expect that $|n\rangle$ and ε_n to be still approximate for H. Let

$$H(\lambda) = H + \lambda V \tag{4.0.12}$$

where $\lambda \in [0, 1]$ allowing us to "slowly turn on" the potential V. We expect that our eigenstates will vary smoothly from $|n\rangle$ at $\lambda = 0$ to $|N\rangle$ at $\lambda = 1$, where $|N\rangle$ is the new eigenvector we wish to find.

That is:

$$(H_0 + \lambda V)|N\rangle = E_n|N\rangle \tag{4.0.13}$$

Let us now expand in powers of λ:

$$|N\rangle = |n\rangle + \lambda\big|N^{(1)}\big\rangle + \lambda^2\big|N^{(2)}\big\rangle + ... \tag{4.0.14}$$

$$E_n = \varepsilon_n + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + ... \tag{4.0.15}$$

> **Warning 4.0:9 (Problems with the Pertubation of a Free Particle)**
>
> Perturbing a free particle with *any* potential will always result in a bad answer.

Let us assume normalization for $|n\rangle$:

$$\langle n \,|\, m\rangle = \delta_{mn} \tag{4.0.16}$$

$$\langle n \,|\, N\rangle = 1 \tag{4.0.17}$$

BUT this does not imply normalization for $|N\rangle$. We in general have:

$$\langle N \,|\, N\rangle \neq 1 \tag{4.0.18}$$

Then

$$\langle n \,|\, N\rangle = 1 = 1 + \lambda\big\langle n \,|\, N^{(1)}\big\rangle + ... \tag{4.0.19}$$

So $\big\langle n \,|\, N^{(i)}\big\rangle = 0$ for $i \neq 0$. By the Schrodinger Equation:

$$(H_0 + \lambda V)|N\rangle = E_n|N\rangle \tag{4.0.20}$$

$$(H_0 + \lambda V)\left[|n\rangle + \sum_i \lambda^i\big|N^{(i)}\big\rangle\right] \tag{4.0.21}$$

$$= \left[\varepsilon_0 + \sum_i \lambda^i E_n^{(i)} \right] \left[|n\rangle + \sum_i \lambda^i |N^{(i)}\rangle \right] \tag{4.0.22}$$

Equate powers of λ

$$\lambda^0 : H_0 |n\rangle = \varepsilon_n |n\rangle \tag{4.0.23}$$

$$\lambda^2 : H_0 |N^{(1)}\rangle + V|n\rangle = \varepsilon_n |N^{(1)}\rangle + E_n^{(1)} |n\rangle \tag{4.0.24}$$

$$\lambda^k : H_0 |N^{(k)}\rangle + V|N^{(k-1)}\rangle = \sum_i^k E_n^{(i)} |N^{(k-i)}\rangle \tag{4.0.25}$$

where

$$E_n^{(0)} = \varepsilon_n \quad ; \quad |N^{(0)}\rangle = |n\rangle \tag{4.0.26}$$

Let's take the scalar product of λ^1 equation with $\langle n|$:

$$\langle n \,|\, H_0 \,|\, N^{(1)} \rangle + \langle n \,|\, V \,|\, n \rangle = \underbrace{\langle n \,|\, \varepsilon_n \,|\, N^{(1)} \rangle}_{0} + \underbrace{\langle n \,|\, E_n^{(1)} \,|\, n \rangle}_{E_n^{(1)}} \tag{4.0.27}$$

Where the 0 term was removed due to orthogonality.

I.e. to find the first order in λ (i.e. in V):

$$E_n = \varepsilon_n + \langle n \,|\, V \,|\, n \rangle \tag{4.0.28}$$

In general:

$$E_n^{(k)} = \langle n \,|\, V \,|\, N^{(k-1)} \rangle \tag{4.0.29}$$

If we know $(k-1)$-th order correction to the wave function, we can obtain kth order correction to energy. Now we just need the correction to the wave function.

4.1.1. Wave Function Corrections

Expand in eigenstates of H_0:

$$|N^{(k)}\rangle = \sum_{m \neq n} |m\rangle \langle m \,|\, N^{(k)} \rangle \quad ; \quad k = 1, 2, \dots \tag{4.1.30}$$

Where $m = n$ is excluded by orthogonality. We now take once again the scalar product of (Eq 25. : @ TimeIndependentPertb) with $\langle m|$ to set expansion coefficients.

For $m \neq n$:

$$\langle m \,|\, H_0 \,|\, N^{(k)} \rangle + \langle m \,|\, V \,|\, N^{(k-1)} \rangle = \sum_i^k E_n^{(i)} \langle m \,|\, N^{(k-i)} \rangle \tag{4.1.31}$$

$$\langle m \,|\, N^{(k)} \rangle = \frac{1}{\varepsilon_n - \varepsilon_m} \left[\langle m \,|\, V \,|\, N^{(k-1)} \rangle - \sum_i^{k-1} E_n^{(i)} \langle m \,|\, N^{k-i} \rangle \right] \tag{4.1.32}$$

So to first order, $k = 1$:

$$\langle m \,|\, N^{(1)} \rangle = \frac{1}{\varepsilon_n - \varepsilon_m} \langle m \,|\, V \,|\, n \rangle \tag{4.1.33}$$

> ### Example 4.1:10 (Helium Ground State)
>
> Let H_H be the Hydrogen Hamiltonian and $V = \frac{\alpha}{R}$ where $\boldsymbol{R} = \boldsymbol{r}_1 - \boldsymbol{r}_2$ and $R = \|\boldsymbol{R}\|$. We have for the Helium atom:
>
> $$H = H_H + V \tag{4.1.34}$$
>
> We know the ground state for H_H is just
>
> $$|n = 0\rangle = \frac{Z^3}{\pi a_0^3} e^{-\frac{Z}{a_0}(r_1 + r_2)} \quad ; \quad Z = 2 \tag{4.1.35}$$
>
> with
>
> $$\varepsilon_0 = -\frac{1}{2} m \alpha^2 [2Z^2] \approx -108.9 \, e\mathrm{V} \tag{4.1.36}$$
>
> Now we calculate the first order ground state energy correction:
>
> $$E_0^{(1)} = \langle n = 0 \,|\, V \,|\, n = 0 \rangle \tag{4.1.37}$$
>
> $$= \int_\infty \mathrm{d}^3(\boldsymbol{x}) \int_\infty \mathrm{d}^3(y) \left(\frac{Z^3}{(\pi a_0^3)^2} \right) \exp\left(-\frac{2Z}{a_0}(r_1 + r_2) \right) \tag{4.1.38}$$
>
> Which we evaluated from a previous leture:
>
> $$\Rightarrow E_0^{(1)} = \frac{1}{2} m \alpha^2 \left[\frac{5}{4} Z \right]_{Z=2} \approx 34.0 \, e\mathrm{V} \tag{4.1.39}$$
>
> $$E_0 = \varepsilon_0 + E_0^{(1)} + O(\text{"}V^2\text{"}) \quad \text{Formally } V^2 \text{ is } \lambda^2 \tag{4.1.40}$$
>
> $$E_0 \approx -74.9 \, e\mathrm{V} \tag{4.1.41}$$
>
> This result is $3.7 \, e\mathrm{V}$ away from the experimental value, $-78.6 \, e\mathrm{V}$.