Approximate Energies for the 2-electron Atom

This is a set of notes on determining the energy of a 2-electron atom in various approximations. In atomic units, the molecular Hamiltonian is:

$$\hat{H} = -\tfrac{1}{2}\nabla_1^2 - \tfrac{Z}{r_1} - \tfrac{1}{2}\nabla_2^2 - \tfrac{Z}{r_2} + \tfrac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \tag{1.1}$$

and if we ignore the electron-electron repulsion term, this is a sum of two hydrogenic Hamiltonians, with ground-state energy

$$E_{\text{no-ee-repulsion}} = -\frac{Z^2}{2n_1^2} - \frac{Z^2}{2n_2^2} \tag{1.2}$$

and wavefunction

$$\Psi_{\text{no-ee-repulsion}} = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_{n_1 l_1 m_1}(\mathbf{r}_1)\sigma_1(1) & \psi_{n_2 l_2 m_2}(\mathbf{r}_1)\sigma_2(1) \\ \psi_{n_1 l_1 m_1}(\mathbf{r}_2)\sigma_1(2) & \psi_{n_2 l_2 m_2}(\mathbf{r}_2)\sigma_2(2) \end{vmatrix} \tag{1.3}$$

For the ground state, this is

$$\begin{aligned} E_{\text{no-ee-repulsion}} &= -\frac{Z^2}{2} - \frac{Z^2}{2} = -Z^2 < E_{g.s.}(\text{true}) \\ \Psi_{\text{no-ee-repulsion}}(\mathbf{r}_1, \mathbf{r}_2) &= \frac{Z^3}{\pi} e^{-Z(r_1+r_2)} \left(\frac{\alpha(1)\beta(2) - \alpha(2)\beta(1)}{\sqrt{2}} \right) \end{aligned} \tag{1.4}$$

This energy must be below the true energy because one has neglected a positive term (the electron-electron repulsion) in the Hamiltonian.

<u>1st-order perturbation theory correction:</u>

Now, to estimate the effect of the electron-electron repulsion using perturbation theory, we add a parameter to the Hamiltonian, writing

$$\hat{H}(\lambda) = -\tfrac{1}{2}\nabla_1^2 - \tfrac{Z}{r_1} - \tfrac{1}{2}\nabla_2^2 - \tfrac{Z}{r_2} + \tfrac{\lambda}{|\mathbf{r}_1 - \mathbf{r}_2|} \tag{1.5}$$

noting that $\hat{H}(\lambda = 0)$ is the "easy" system we just solved and $\hat{H}(\lambda = 1)$ is the true physical system we want to solve. Then, at the level of first-order perturbation theory,

$$E(\lambda) = E(0) + \lambda \left.\frac{dE}{d\lambda}\right|_{\lambda=0} \tag{1.6}$$

and for the $\lambda = 1$ case of interest,

$$E(1) = E_{\text{1-orderPT}} = E(0) + \left.\frac{dE}{d\lambda}\right|_{\lambda=0} \tag{1.7}$$

and, from the Hellmann-Feynman theorem,

$$\begin{aligned} \left.\frac{dE}{d\lambda}\right|_{\lambda=0} &= \int \Psi^*_{\text{no-ee-repulsion}}(\mathbf{r}_1, \mathbf{r}_2) \frac{d\hat{H}}{d\lambda} \Psi_{\text{no-ee-repulsion}}(\mathbf{r}_1, \mathbf{r}_2)\, d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \frac{Z^6}{\pi^2} \iint \frac{e^{-Z(\mathbf{r}_1+\mathbf{r}_2)} e^{-Z(\mathbf{r}_1+\mathbf{r}_2)}}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \frac{5}{8} Z \end{aligned} \tag{1.8}$$

The last integral I am *giving* to you. (I don't expect you to be able to solve it, at least not in the limited time allowed on an exam.)

So the energy of the 2-electron atom is

$$E_{\text{1-orderPT}} = -Z^2 + \frac{5}{8}Z > E_{g.s.}(\text{true}) \tag{1.9}$$

I know this is greater than the true ground-state energy because

$$E_{\text{1-orderPT}} = \iint \Psi^*_{\lambda=0}(\mathbf{r}_1,\mathbf{r}_2)\hat{H}\Psi_{\lambda=0}(\mathbf{r}_1,\mathbf{r}_2)\,d\mathbf{r}_1 d\mathbf{r}_2 > E_{g.s.}(\text{true}) \tag{1.10}$$

based on the variational principle.

<u>Variational Refinement:</u>

Now we can imagine trying to refine the wavefunction using an effective nuclear charge. The new wavefunction we consider is

$$\Psi_\zeta(\mathbf{r}_1,\mathbf{r}_2) = \frac{\zeta^3}{\pi}e^{-\zeta(r_1+r_2)}\left(\frac{\alpha(1)\beta(2)-\alpha(2)\beta(1)}{\sqrt{2}}\right) \tag{1.11}$$

which we notice is the *exact* wavefunction for the Hamiltonian *without* any electron-electron repulsion with nuclear charge ζ,

$$\hat{H}_{\text{no-ee-repulsion}}(\zeta) = -\tfrac{1}{2}\nabla_1^2 - \tfrac{\zeta}{r_1} - \tfrac{1}{2}\nabla_2^2 - \tfrac{\zeta}{r_2} \tag{1.12}$$

Merely substituting Eq. (1.11) into (1.8) gives the expectation value for the electron-electron repulsion as

$$\begin{aligned}\langle V_{ee}\rangle &= \int \Psi^*_\zeta(\mathbf{r}_1,\mathbf{r}_2)\frac{1}{|\mathbf{r}_1-\mathbf{r}_1|}\Psi_\zeta(\mathbf{r}_1,\mathbf{r}_2)\,d\mathbf{r}_1 d\mathbf{r}_2\\ &= \frac{\zeta^6}{\pi^2}\iint \frac{e^{-\zeta(\mathbf{r}_1+\mathbf{r}_2)}e^{-\zeta(\mathbf{r}_1+\mathbf{r}_2)}}{|\mathbf{r}_1-\mathbf{r}_2|}\,d\mathbf{r}_1 d\mathbf{r}_2\\ &= \frac{5}{8}\zeta\end{aligned} \tag{1.13}$$

To determine the other contributions to the energy, note that from the Hellmann-Feynman theorem,

$$\begin{aligned}\frac{dE_{\text{no-ee-repulsion}}(\zeta)}{d\zeta} &= \int \Psi^*_{\text{no-ee-repulsion}}(\mathbf{r}_1,\mathbf{r}_2)\frac{d\hat{H}_{\text{no-ee-repulsion}}(\zeta)}{d\zeta}\Psi_{\text{no-ee-repulsion}}(\mathbf{r}_1,\mathbf{r}_2)\,d\mathbf{r}_1 d\mathbf{r}_2\\ \frac{d\left(\frac{-\zeta^2}{n^2}\right)}{d\zeta} &= \frac{\zeta^6}{\pi^2}\iint e^{-\zeta(\mathbf{r}_1+\mathbf{r}_2)}\left(-\frac{1}{r_1}-\frac{1}{r_2}\right)e^{-\zeta(\mathbf{r}_1+\mathbf{r}_2)}\,d\mathbf{r}_1 d\mathbf{r}_2\\ \frac{-2\zeta}{n^2} &= \frac{\zeta^6}{\pi^2}\iint e^{-\zeta(\mathbf{r}_1+\mathbf{r}_2)}\left(-\frac{1}{r_1}-\frac{1}{r_2}\right)e^{-\zeta(\mathbf{r}_1+\mathbf{r}_2)}\,d\mathbf{r}_1 d\mathbf{r}_2\end{aligned} \tag{1.14}$$

Notice, now, that the electron-nuclear attraction integral is

$$\begin{aligned}\langle V_{ne}\rangle &= \left\langle -\frac{Z}{r_1}-\frac{Z}{r_2}\right\rangle = \frac{\zeta^6}{\pi^2}\iint e^{-\zeta(\mathbf{r}_1+\mathbf{r}_2)}\left(-\frac{Z}{r_1}-\frac{Z}{r_2}\right)e^{-\zeta(\mathbf{r}_1+\mathbf{r}_2)}d\mathbf{r}_1 d\mathbf{r}_2\\ &= Z\frac{\zeta^6}{\pi^2}\iint e^{-\zeta(\mathbf{r}_1+\mathbf{r}_2)}\left(-\frac{1}{r_1}-\frac{1}{r_2}\right)e^{-\zeta(\mathbf{r}_1+\mathbf{r}_2)}d\mathbf{r}_1 d\mathbf{r}_2\\ &= \frac{-2Z\zeta}{n^2}\end{aligned} \tag{1.15}$$

The kinetic-energy integral could also be determined from the Hellman-Feynman theorem (use non-atomic-units and differentiate with respect to $\hbar$). However, for the exact Hamiltonian, we know that

$$\begin{aligned}E_{\text{no-ee-repulsion}}(\zeta) = -\frac{\zeta^2}{n^2} &= \langle T\rangle + \langle V_{ne}(\zeta)\rangle\\ -\frac{\zeta^2}{n^2} &= \langle T\rangle - \frac{2\zeta^2}{n^2}\\ \langle T\rangle &= \frac{\zeta^2}{n^2}\end{aligned} \tag{1.16}$$

So the energy expression we have is:

$$\begin{aligned}E(\zeta) &= \int \Psi^*_{\text{no-ee-repulsion}}(\mathbf{r}_1,\mathbf{r}_2)\hat{H}_{\text{no-ee-repulsion}}(\zeta)\Psi_{\text{no-ee-repulsion}}(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2\\ &= \langle T\rangle + \langle V_{ne}(Z)\rangle + \langle V_{ee}\rangle\\ &= \zeta^2 - 2\zeta Z + \tfrac{5}{8}\zeta\end{aligned} \tag{1.17}$$

We find the optimal effective nuclear charge by differentiation this expression,

$$\begin{aligned}0 = \tfrac{dE}{d\zeta} &= 2\zeta - 2Z + \tfrac{5}{8}\\ \zeta &= Z - \tfrac{5}{16}\end{aligned} \tag{1.18}$$

Substituting this expression into Eq. (1.17) gives the best variational energy (which is still above the true energy),

$$\begin{aligned}E(\zeta_{\min}) &= \left(Z-\tfrac{5}{16}\right)^2 - 2Z\left(Z-\tfrac{5}{16}\right) + \tfrac{5}{8}\left(Z-\tfrac{5}{16}\right)\\ &= \left(Z-\tfrac{5}{16}\right)\left(\left(Z-\tfrac{5}{16}\right) - 2Z + \tfrac{5}{8}\right)\\ &= -\left(Z-\tfrac{5}{16}\right)\left(-Z+\tfrac{5}{16}\right)\\ &= -\left(Z-\tfrac{5}{16}\right)^2\end{aligned} \tag{1.19}$$