1. FIG. 1 A sketch of the energy level diagram for Helium. The Aufbau principle’s \( n + l \) rule determines that 2s is lower than 2p, and Hund’s rules determine the splitting of the terms (e.g. larger \( S \)).

2. By the virial theorem, \( 2T = -V_{ee} - V \) and \( E = \frac{1}{2}(V_{ee} + V) \). The integral \( X = \int d^3r\, u(x) \) is related to the external potential energy by \( X = -\frac{V_{ee}}{Z} \), where \( Z = 10 \) for Ne.

\[
X = -\frac{2E - V_{ee}}{Z} = -56.9
\]

3. Using the exact ground-state energy given in the previous question, the correlation energy is \( E_C = E - E_{HF} = -0.39 \). Ne has 10 electrons so the correlation is about \(-0.039 = -1.06 \text{ eV per electron} \) (the 1 eV correlation energy per electron rule is surprisingly accurate). Since the ionization potential is a difference of energies, the correlation for the remaining 9 electrons cancels. Thus the error \( I_{\text{exact}} - I_{\text{HF}} \approx 0.04 \), the correlation energy for one electron (remember that HF underestimates the ionization potential). Compare with the exact error 0.064.

4. \( \epsilon_\pm = \alpha \pm \beta \), where \( \alpha = -2 \), the diagonal elements, and \( \beta = -1 \), the off-diagonal elements. The ground-state energy is \( \epsilon_+ = -3 \).

5. The virial theorem gives

\[
2T = \langle x \frac{\partial V}{\partial x} \rangle = \langle x^2 + x^4 \rangle
\]

Note that this is not related to \( V \) like in most cases.

6. \( \phi_1(x) = x, \phi_2(x) = x^2 \) and \( \phi_3(x) = 1 \).

\[
\Psi(x, y, z) = \frac{1}{\sqrt{3!}} \begin{vmatrix} x & y & z \\ x^2 & y^2 & z^2 \\ 1 & 1 & 1 \end{vmatrix}
\]

This simplifies to \( \Psi(x, y, z) = -\frac{1}{\sqrt{6}}(x - y)(x - z)(y - z) \).

7. (a) \( V_{ee} > 0 \).
(b) \( U > 0 \).
(c) \( V_{ee} - U = E_X < 0 \).

8. For large \( D \), the particle doesn’t see the infinite walls at \( x = 0 \) and \( x = 1 \), so we can just treat it like a harmonic oscillator. Get the potential into a form we recognize by substituting \( x \to u + \frac{1}{2} \)

\[
V = -Dx(1 - x) = D(u + \frac{1}{2})(u - \frac{1}{2}) = Du^2 - \frac{D}{4}
\]
The constant term is the bottom of the well. Thus \( \frac{1}{2} m \omega = D \implies \omega = \sqrt{\frac{2D}{m}} \). The ground state is

\[
E_0 = \frac{1}{2} \omega - \frac{D}{4} = \sqrt{\frac{D}{2m}} - \frac{D}{4} \tag{6}
\]

9.

Cr is an exception to the Aufbau principle because 4s and 3d are so close in energy that promoting one electron out of 4s to form a half filled d-shell is energetically favorable. A half-filled d-shell is more stable because the parallel spins can interact via an exchange energy, lowering the overall energy (anti-parallel spins do not contribute to the exchange energy).

10.

DFT is not variational, so the variational principle doesn’t apply here. The virial theorem is a measure of how close the ground-state energy is to the exact value, so in cc-pv5z the virial theorem will be more closely satisfied because the error is less.