22.1.

1.

This is just the solution to a particle in a box. Eigenfunctions and eigenenergies are

\[ \phi_n(x) = \begin{cases} \sqrt{\frac{2}{a}} \cos \left( \frac{(n+1)\pi x}{a} \right) & \text{if } n = 0, 2, 4, \ldots \\ \sqrt{\frac{2}{a}} \sin \left( \frac{(n+1)\pi x}{a} \right) & \text{if } n = 1, 3, 5, \ldots \end{cases} \]

\[ \epsilon_n = \frac{\hbar^2 \pi^2 (n + 1)^2}{2ma^2} \]  

(1)

2.

Use first-order perturbation theory \( \Delta \epsilon_n^{(1)} = \langle \phi_n | v | \phi_n \rangle \)

\[ \Delta \epsilon_n^{(1)} = \begin{cases} -\frac{D}{2} \left( 1 + \frac{2}{\pi (n+1)} \right) & \text{if } n = 0, 2, 4, \ldots \\ -\frac{D}{2} & \text{if } n = 1, 3, 5, \ldots \end{cases} \]  

(2)

The correction to the even energies are larger than those to the odd energies because the even state resides in the perturbation more. As \( n \to \infty \), the correction to the even energies approaches \(-D/2\). For odd \( n \), the correction is always \(-D/2\) because the width of the well is exactly half, and so the same amount resides in the perturbation for all \( n \). For the approximate solution to be accurate, the perturbation \( D \) should be smaller than the unperturbed ground state energy.

3.

For very large \( D \), the perturbation becomes the infinite well; this is just a particle in a box with width \( a/2 \). The new energy levels are \( v(x) = -D \) relative to the original well level.

\[ \epsilon'_n = \frac{\hbar^2 \pi^2 (n + 1)^2}{2ma^2} - D \]  

(3)

At the edges of the well of width \( a/2 \), there is exponential leakage of the density into the original well, which should require an exponential correction to the energy (on the order of \( \sim e^D \)).

4.

Construct the matrix elements \( H_{ij} = \langle \phi_i | \hat{H} | \phi_j \rangle \) for \( i, j = 0, 2 \) (e.g. the ground and second excited states).

\[ \begin{bmatrix} \epsilon_0 + \Delta \epsilon_0^{(1)} & -\frac{D}{\pi} \\ -\frac{D}{\pi} & \epsilon_2 + \Delta \epsilon_2^{(1)} \end{bmatrix} \]

(4)

The lowest eigenvalue is an estimate for the new ground state energy.

\[ \epsilon_0'' = \frac{1}{6\pi m^2 a^4} \left( 15\pi^3 \hbar^2 ma^2 - (2 + 3\pi)ma^2 D \right) - 2\sqrt{m^2 a^4 (13m^2 a^4 D^2 + 24\pi^2 \hbar^2 ma^2 D + 36\pi^6 \hbar^4)} \]  

(5)

We can expand this expression in orders of \( D \)

\[ \epsilon_0'' = \frac{\hbar^2 \pi^2}{2ma^2} - \frac{(2 + \pi)D}{2\pi} - \frac{ma^2 D}{4\pi^3 \hbar^2} + \ldots \]  

(6)

For \( D = 0 \) we recover the unperturbed ground state energy. Notice that the linear correction is the same as the correction we got using first-order perturbation theory. Now, however, we get second- and higher-order corrections to the ground state energy.

5.

Solving for \( D \) when \( \epsilon_0'' = 0 \), we find

\[ D = \frac{\pi^3 \hbar^2 \left( 26 + 15\pi - 2\sqrt{277 + 12\pi(14 + 3\pi)} \right)}{ma^2 (\pi(4 + 3\pi) - 16)} = 5.92711 \frac{\hbar^2}{ma^2} \]  

(7)

6.

The exact problem can be solved numerically for arbitrary \( D \) in Mathematica using a shooting method. For zero total energy, the ground state can be found analytically by solving the Schrodinger equation (in the unperturbed regions, the wavefunction is linear). Figure 1 shows the exact ground state energy as a function of the perturbation depth \( D \). Our estimate is very good, but breaks down when \( D \) becomes large as expected.

Figure 2 compares the unperturbed ground state wavefunction with the exact solution for two different values of \( D \). \( D = 6 \) corresponds to zero total energy. As \( D \) grows large, the exact wavefunction moves into the inner well because the potential is lower there.
2.
(a) 27.2 eV = 1 Ha
(b) 23.06 kcal/mol = 1 eV
(c) 4.184 kJ/mol = 1 kcal/mol
(d) 83.59 cm\(^{-1}\) = 1 kJ/mol
(e) 1.4388 K = 1 cm\(^{-1}\)

3.
(a) \(m_p = 1836.2\)
(b) \(c = 137.04\)
(c) \(I_{\text{He}} = 24.587\) eV
(d) \(\Delta Cl = -349\) kJ/mol
(e) 436 kJ/mol
(f) \{3657, 1595, 3756\} cm\(^{-1}\)
(g) 1.85 kcal/mol
(h) 2.07 kcal/mol

4.
Our Hamiltonian does not depend on the nuclear coordinates, so we are using the Born-Oppenheimer approximation
\[
\hat{H}_{\text{He}} = -\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{|r_1 - r_2|} \quad (9)
\]

5.
Trends: the more bonds, the greater the bond energy; the smaller the bond length, the greater the bond energy.

6.
Rewrite all our answers in terms of the parameter \(\gamma = \frac{\hbar^2}{ma^2} = 0.06996\) Ha for \(a = 2\) Å.
\[
\epsilon_n = \frac{\pi^2(n+1)^2}{2} \gamma \quad (10)
\]
\[
\epsilon'_n = 2\pi^2(n+1)^2\gamma - D \quad (11)
\]
\[
\epsilon''_0 = \frac{5}{2} \pi^2 \gamma - \frac{(2+3\pi)}{6\pi} D - \frac{1}{3} \sqrt{\frac{13}{3} D^2 + 24\pi D + 36\pi^4 \gamma^2} \quad (12)
\]
\[ D = 5.92711 \gamma \]  \hspace{1cm} (13)

The important dimensionless parameter is the ratio \( D \gamma = 5.92711 \). This parameter, which determines at what \( D \) the total energy changes sign, tells us the crossover point between the energy scales of the perturbation and the unperturbed ground state energy.

22.3.

1. The model Hamiltonian matrix for \( H_2 \) is

\[ H = \begin{bmatrix} \alpha & \beta \\ \beta & \alpha \end{bmatrix}, \]  \hspace{1cm} (14)

where \( \alpha = -13.6 \text{ eV} \). Solve for \( \beta \)

\[ E_{H_2} = 2E_H - E_{\text{bond}} \]
\[ 2(\alpha + \beta) = 2\alpha - 4.52 \text{ eV} \]  \hspace{1cm} (15)
\[ \beta = -2.26 \text{ eV} \]  \hspace{1cm} (16)

2.

\( \beta \) is the matrix element of the Hamiltonian with the two wavefunctions of the two H atoms (e.g. \( \beta = \langle a | H | b \rangle \)). If the distance \( R \) between the nuclei becomes 0, then we have a Helium atom and \( |a\rangle = |b\rangle \), which means that \( \alpha = \beta \). If \( R \rightarrow \infty \), then the overlap between \( |a\rangle \) and \( |b\rangle \) becomes 0 and we have \( \beta = 0 \).

3.

Yes, when you add the energy due to the repulsion between the nuclei to the total ground state electronic energy, you will get a typical binding energy curve.

4. Energy of the first excited state

\[ E_1 = (\alpha + \beta) + (\alpha - \beta) = 2\alpha \]  \hspace{1cm} (17)

5.

Construct the Hamiltonian matrix again

\[ H = \begin{bmatrix} \alpha_1 & \beta \\ \beta & \alpha_2 \end{bmatrix}, \]  \hspace{1cm} (18)

The lowest eigenvalue is

\[ E_0 = \frac{1}{2} \left( \alpha_1 + \alpha_2 - \sqrt{\alpha_1^2 - 2\alpha_1\alpha_2 + \alpha_2^2 + 4\beta^2} \right). \]  \hspace{1cm} (19)

The dissociation energy is given by solving \( \Delta E = (\alpha_1 + \alpha_2) - 2E_0 \). Given \( \alpha_1 = -5.38 \text{ eV} \), we find \( \Delta E = -9.38 \text{ eV} \), which is far off from the experimental value -2.5 eV.

6.

Construct a 3x3 matrix this time, assuming the end H atoms don’t interact with each other

\[ H = \begin{bmatrix} \alpha & \beta & 0 \\ \beta & \alpha & \beta \\ 0 & \beta & \alpha \end{bmatrix}, \]  \hspace{1cm} (20)

The eigenvalues are \( \alpha, \alpha - \beta\sqrt{2}, \alpha + \beta\sqrt{2} \). The bound molecule occupies the two lowest states, so the dissociation energy is given by

\[ \Delta E = 3\alpha - (\alpha + \alpha - \beta\sqrt{2}) = \alpha + \beta\sqrt{2} \]  \hspace{1cm} (21)

This is more negative than the dissociation energy for 3 \( H_2 \), which is 6\( \beta \), so therefore 3 \( H_2 \) is more stable than 2 \( H_3 \).