The Born Oppenheimer (BO) Approximation for Molecular Structure [Atkins, Chapt. 8]

Consider the hydrogen (H₂) Molecule:
The full electro-nuclear Schrödinger Eq. reads:

\[ H\Psi(\vec{r}_1, \vec{r}_2, \vec{R}_A, \vec{R}_B) = E\Psi(\vec{r}_1, \vec{r}_2, \vec{R}_A, \vec{R}_B) \]

\[ H = \sum_{\alpha=A,B} -\frac{\hbar^2}{2m_p} \nabla^2_\alpha + \sum_{j=1,2} -\frac{\hbar^2}{2m_e} \nabla^2_j - \frac{e_0^2}{4\pi\varepsilon_0 r_1A} - \frac{e_0^2}{4\pi\varepsilon_0 r_1B} - \frac{e_0^2}{4\pi\varepsilon_0 r_2A} - \frac{e_0^2}{4\pi\varepsilon_0 r_2B} + \frac{e_0^2}{4\pi\varepsilon_0 r_{12}} + \frac{e_0^2}{4\pi\varepsilon_0 R_{AB}} \]
According to the Born-Oppenheimer Approx.: 

$$\Psi(\vec{r}_1, \vec{r}_2, \vec{R}_A, \vec{R}_B) \approx \psi_j(\vec{r}_1, \vec{r}_2; \vec{R}_A, \vec{R}_B) \chi^{(n)}(\vec{R}_A, \vec{R}_B)$$

Here:

$$H_{el} \psi_j(\vec{r}_1, \vec{r}_2; \vec{R}_A, \vec{R}_B) = E^{(j)}(\vec{R}_A, \vec{R}_B) \psi_j(\vec{r}_1, \vec{r}_2; \vec{R}_A, \vec{R}_B)$$

$$H_{el} = \sum_{j=1,2} \frac{-\hbar^2}{2m_e} \nabla^2_j - \frac{e_0^2}{4\pi\varepsilon_0 r_{1A}} - \frac{e_0^2}{4\pi\varepsilon_0 r_{1B}} - \frac{e_0^2}{4\pi\varepsilon_0 r_{2A}} - \frac{e_0^2}{4\pi\varepsilon_0 r_{2B}} + \frac{e_0^2}{4\pi\varepsilon_0 r_{12}} + \frac{e_0^2}{4\pi\varepsilon_0 R_{AB}}$$

Then:

$$H_{nuc} \chi(\vec{R}_A, \vec{R}_B) = E^{(j)}(\vec{R}_A, \vec{R}_B) \chi(\vec{R}_A, \vec{R}_B)$$

with:

$$H_{nuc} = \sum_{\alpha=A,B} \frac{-\hbar^2}{2m_p} \nabla^2_{\alpha} + E_{el}^{(j)}(\vec{R}_A, \vec{R}_B)$$
For the hydrogen molecule (or any diatomic):

\[ E_{el}^{(j)}(\vec{R}_A, \vec{R}_B) = E_{el}^{(j)}(\mid \vec{R}_A - \vec{R}_B \mid) \]

Plotting, schematically:
Then, the total energy (eigenvalue) of the molecule (excluding translation of the molecular center of mass) is given by:
Atkins’ “derivation” of the BO approximation (Sect. 8.1):

\[
H = -\frac{\hbar^2}{2m_e} \frac{\partial^2}{\partial z^2} - \sum_{j=1,2} \frac{\hbar^2}{2m_j} \frac{\partial^2}{\partial Z_j^2} + V(z, Z_1, Z_2)
\]

\[
H = T_e + T_N + V
\]

Full electro-nuclear Hamiltonian (collinear reduction)

\[
H\Psi(z, Z_1, Z_2) = E\Psi(z, Z_1, Z_2)
\]

Full electro-nuclear Schrodinger Eq.

\[
\Psi(z, Z_1, Z_2) = \psi(z; Z_1, Z_2) \chi(Z_1, Z_2)
\]

Presumed Born-Oppenheimer (BO) factorization of the wavefunction.

\[
H\psi\chi = \chi T_e \psi + \psi T_N \chi + V \psi \chi + W = E\psi\chi
\]

Substitution of BO wavefunction Ansatz into (full) SE.

\[
W = \sum_{j=1,2} \frac{\hbar^2}{2m_j} \left( 2 \frac{\partial \psi}{\partial Z_j} \frac{\partial \chi}{\partial Z_j} + \frac{\partial^2 \psi}{\partial Z_j^2} \chi \right)
\]

Non-adiabatic coupling terms..
Assuming that the non-Born Oppenheimer terms (i.e., W) are tiny:

\[ \chi T_e \psi + \psi T_N \chi + V \psi \chi = E \psi \chi \]  \hspace{1cm} [1]

\[ \psi T_N \chi + (T_e \psi + V \psi) \chi = E \psi \chi \]  \hspace{1cm} \text{Rearrange Eq. [1]}

\[ T_e \psi + V \psi = E_e (Z_1, Z_2) \psi \]  \hspace{1cm} \text{Solve the electronic SE for fixed ("frozen")}

\[ \psi T_N \chi + E_e \psi \chi = E \psi \chi \]  \hspace{1cm} \text{Substitute the solution for the electronic SE into Eq. [1]}

\[ T_N \chi + E_e \chi = E \chi \]  \hspace{1cm} \text{This implies the indicated nuclear coordinate Schrod. Eq.}
A (semi)quantitative example of chemical bonding: \( H_2^+ \)

For nuclei A,B clamped at internuclear separation \( R^{**} \), the electronic Hamiltonian reads:

\[
\hat{H} = -\frac{\hbar^2}{2m_e} \nabla^2 + \frac{e^2}{4\pi\varepsilon_0 R} - \frac{e^2}{4\pi\varepsilon_0 r_A} - \frac{e^2}{4\pi\varepsilon_0 r_B}
\]

** i.e., within the Born-Oppenheimer approx.
A reasonable approximation to the (unnormalized) ground electronic state energy eigenfunction turns out to be:

\[ \psi_{gs}(\vec{r}) = 1s_A(\vec{r}) + 1s_B(\vec{r}) \]
Thus:

\[
E_{gs}(R) \approx \frac{\int d\vec{r} \psi_{gs}(\vec{r}) H \psi_{gs}(\vec{r})}{\int d\vec{r} \psi_{gs}^2(\vec{r})} = -\frac{1}{2} + \frac{J'(R) + K'(R)}{1 + S(R)}
\]

where \( R \) is in units of the Bohr radius \( a_0 \); \( E \) is in units of Hartrees: 1 Hartree = \( 2 \times 13.6 \text{eV} = 27.2 \text{eV} \).

Furthermore, \( J'(R) \), \( K'(R) \), \( S(R) \) are simple (known!) functions, all of which vanish as \( R \to \infty \).
$S$, $J', K'$ represent the integrals:

\[ S = \int d\vec{r} 1s_A 1s_B \]

\[ J' = \int d\vec{r} 1s_A \left( -\frac{1}{r_B} + \frac{1}{R} \right) 1s_A \]

\[ K' = \int d\vec{r} 1s_A \left( -\frac{1}{r_A} + \frac{1}{R} \right) 1s_B \]

These integrals evaluate to:

\[ S(R) = e^{-R} \left( 1 + R + \frac{R^2}{3} \right) \]

\[ J'(R) = e^{-2R} (1 + \frac{1}{R}) \]

\[ K'(R) = \frac{S(R)}{R} - e^{-R} (1 + R) \]

where $R$ is measured in units of the Bohr radius, $a_0=0.53$ Å, and $J'$, $K'$ are measured in terms of the Hartree (or atomic unit = a.u. of energy), 1 Hartree = 27.2 eV.
Finally, a reasonable approximation to the (unnormalized) 1st excited electronic state energy eigenfunction turns out to be:

\[
\psi_{es}(\vec{r}) = 1s_A(\vec{r}) - 1s_B(\vec{r})
\]
One then evaluates:

\[
E_{es}(R) \cong \frac{\int d\vec{r} \psi_{es}(\vec{r}) \hat{H} \psi_{es}(\vec{r})}{\int d\vec{r} \psi_{es}^2(\vec{r})} = -\frac{1}{2} + \frac{J'(R) - K'(R)}{1 - S(R)}
\]
Additional Comments on the H$_{2}^{+}$ molecule ion:

1) The Schrödinger Eq. for this problem can be solved analytically in elliptical coordinates:

The analytical expressions for $\psi, E$ are “too complicated” to present here. (The same essential content is contained in the simple 1sA,1sB molecular orbital analysis given above.)

However, the elliptical coordinate transformation can be used to evaluate $S(R), J'(R), K'(R)$ analytically (see above).
2) Here is a more quantitative diagram of the bonding (ground state) and anti-bonding (excited state) nuclear potential energy curves obtained from the simple 1sA,1sB MO treatment above:

These curves are in semi-quantitative agreement with exact solutions of H2+ molecule Schrodinger Eq. (which agree well with spectroscopic data).