Griffiths uses the variational chapter as a way to discuss Molecular Orbitals (ie PE involves separated nuclei — no spherical symmetry). So in the context of H_2^+ (one electron, two separated nuclei) we will have a wavefunction that surrounds both nuclei.

Note: H_2^+ can be "exactly" solved - but it is way too complex for any classroom. Hence approximation.

An old-fashion (but not very accurate) approach is to make our Molecular orbit by a LCAO [linear combination of atomic orbitals]. No adjustable parameters in this version just calculate $\langle H \rangle$ & know the answer is above the actual ground state.

Even this simple approach is too much for the blackboard so we go back to 1d with δ function potentials.

Recall in dimensionless coordinates:

$H = -\frac{1}{2}\partial_x^2 - \delta(x)$: 1 bound state $H\psi = E\psi$ $E = -\frac{1}{2}$, $\psi \propto e^{-|x|}$

In our 1d, δ-function version of H_2^+ we make a linear combination of a "atomic" solution on the nucleus at $x = -a$ [call this $f_-(x)$] and an "atomic" solution at $x = +a$ [call this $f_+(x)$]

Trial $\psi = [f_+(x) \pm f_-(x)] = e^{-|x-a|} \pm e^{-|x+a|}$

Remark: in the web version the δ-functions are at $\pm\frac{a}{2}$ so a = separation; then $2a$ = separation.

$H = -\frac{1}{2}\partial_x^2 - \delta(x-a) - \delta(x+a) = -\frac{1}{2}\partial_x^2 + V_+(x) + V_-(x)$

Potential for a nucleus at $x = +a$

$$\langle\psi|H|\psi\rangle = \int (f_+ \pm f_-)\left[-\tfrac{1}{2}\partial_x^2 + V_+ + V_-\right](f_+ \pm f_-)\,dx$$

($E f_-$ and $E f_+$)

$$= \int E f_+ f_+ + f_+ V_- f_+ \pm f_+ E f_- \pm f_+ V_+ f_- + E f_- f_- + f_- V_+ f_- \pm f_- E f_+ \pm f_- V_- f_+ \; dx$$

- $E f_- f_-$: normalized $\equiv E$
- $f_- V_+ f_-$: equal $\equiv$ direct $\equiv D$
- $f_- E f_+$: equal $\equiv$ overlap $\equiv I$
- $f_- V_- f_+$: equal $\equiv$ exchange $\equiv X$

$$= 2\{E + D \pm EI \pm X\}$$

$$\langle\psi|\psi\rangle = \int (f_+ \pm f_-)^2\,dx = \int f_+^2 \pm 2 f_+ f_- + f_-^2\,dx$$

$$= 2\{1 \pm I\}$$

$$\frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{E(1 \pm I) + D \pm X}{1 \pm I} = E + \frac{D \pm X}{1 \pm I}$$

Note: In the limit of widely spaced nuclei: overlap small

and $D, X, I \to 0 \Rightarrow E \to 0$ (correct)

In the limit of closely spaced nuclei: $f_+ = f_-$; $V_+ = V_-$

$D = X = \langle V\rangle$; $I = 1$ (this result is not usually accurate)

$$I = \int e^{-|x-a|} e^{-|x+a|}\,dx = 2\left[\int_0^a e^{-(x+a)} e^{x-a}\,dx + \int_a^\infty e^{-(x+a)} e^{a-x}\,dx\right]$$

$e^{-(x+a)} e^{x-a} = e^{-2a} \Rightarrow a e^{-2a}$

$e^{-(x+a)} e^{a-x} = e^{-2x} \Rightarrow -\tfrac{1}{2} e^{-2x}\Big|_a^\infty = \frac{e^{-2a}}{2}$

$$= 2\left[a + \tfrac{1}{2}\right]e^{-2a}$$

→ check: goes to zero as $a \to \infty$; goes to 1 as $a \to 0$

$$D = -\int \delta(x+a)\, e^{-|x-a|^2}\,dx = -e^{-4a}$$

→ check: goes to zero as $a \to \infty$; goes to $\langle V\rangle$ as $a \to 0$

$$X = -\int \delta(x+a)\, e^{-|x-a|} e^{-|x+a|}\,dx = -e^{-2a}$$

→ yes

$$\frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} = E^{-\frac{1}{2}} + \frac{-e^{-4\rho} \pm e^{-2\rho}}{1 \pm (2\rho+1)e^{-2\rho}}$$

This is "electronic" energy → should add proton repulsion — say $\frac{1/4}{(2a)^2}$

Remark: Griffiths gives results for real H_2^+ — it's all the same except now 3d integrals w. th Coulomb potential

Another problem we can attempt is $2e^-$ atoms eg He

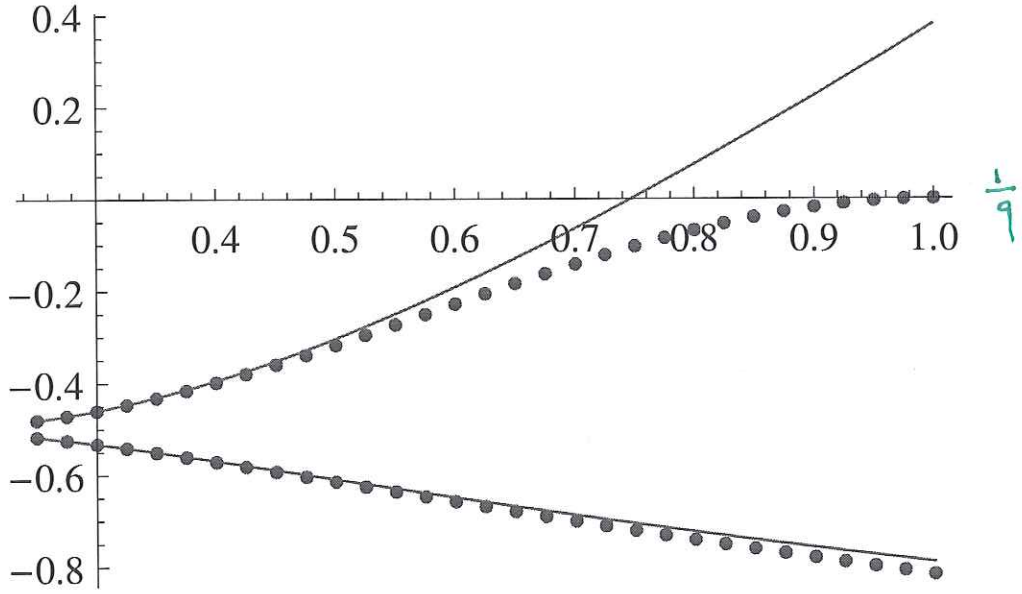
The "perturbation" is the $e^- e^-$ repulsion: $\frac{e^2}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|}$

H.06.html works this problem using the atomic orbitals (no adjustable parameters) without concern for fermion behavior

H.07.html does the $\langle H \rangle$ calculation for properly symmetric (spin singlet) and antisymmetric (spin triplet) states. Again — no adjustable parameters

Note: as you might imagine, $\left\langle \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right\rangle$ is the hard part of these calculations.

Note: the poss. ble existence of H^- (2 e^-, 1 proton) was a particular concern. This topic is taken up in H.13.html #17 - #19. As stated there, a good theoretical value demands making the wf pay attention to the actual distance between the electrons ie $|\vec{r}_1 - \vec{r}_2|$ not just $r_1 - r_2$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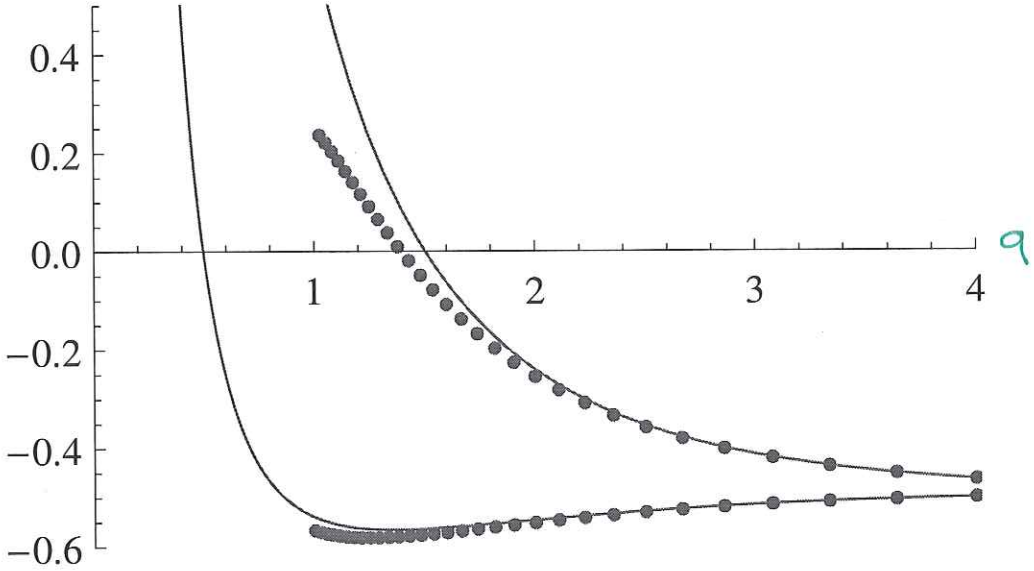
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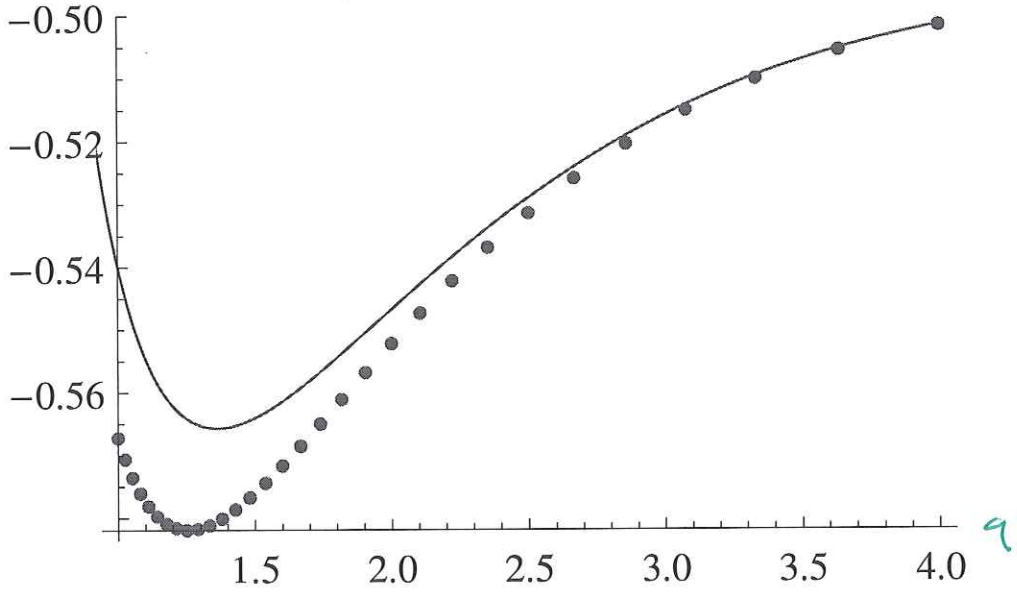
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