Physics 522: Quantum II

Problem Set # 7 Solutions

Problem 1:

The "exchange interaction" between identical spin-½ particles can be used to swap the spin state stored at one location with that in another. To see this, consider the exchange Hamiltonian

$$\hat{H} = \underset{\substack{\Uparrow \\ \text{exchange coupling strength}}}{J}\, \hat{\vec{S}}_1 \cdot \hat{\vec{S}}_2$$

This is a shorthand notation for

$$\hat{H} = \frac{J}{4}\left\{ \underset{\substack{\uparrow \\ \text{particle 1}}}{\hat{\sigma}_x} \otimes \underset{\substack{\uparrow \\ \text{particle 2}}}{\hat{\sigma}_x} + \hat{\sigma}_y \otimes \hat{\sigma}_y + \hat{\sigma}_z \otimes \hat{\sigma}_z \right\}$$

In the standard by $\{|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle\}$

$$\hat{\sigma}_x \otimes \hat{\sigma}_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \otimes \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix}$$

$$\hat{\sigma}_y \otimes \hat{\sigma}_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \otimes \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{bmatrix}$$

$$\hat{\sigma}_z \otimes \hat{\sigma}_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \otimes \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

$$\Rightarrow \hat{H} = \frac{J}{4}\begin{bmatrix}1&0&0&0\\0&-1&2&0\\0&2&-1&0\\0&0&0&1\end{bmatrix}$$

(b) Now we seek $\hat{U}(t) = e^{-\frac{i}{\hbar}\hat{H}t}$

Two exponentiate the Hamiltonian, the general thing to do is first diagonalize $\hat{H}$

- We see that $|\uparrow\uparrow\rangle$ and $|\downarrow\downarrow\rangle$ are eigenvectors with the same eigenvalue $J/4$

- We need to diagonalize the block

$$\hat{H} = \frac{J}{4}\begin{array}{cc}\begin{bmatrix}-1&2\\2&-1\end{bmatrix} & \begin{array}{c}|\uparrow\downarrow\rangle\\|\downarrow\uparrow\rangle\end{array}\end{array}$$

The eigenvectors are $|\pm\rangle = \frac{|\uparrow\downarrow\rangle \pm |\downarrow\uparrow\rangle}{\sqrt{2}}$

with eigenvalue $-\frac{J}{4} \pm \frac{J}{2} = \left(\frac{J}{4}, -\frac{3J}{4}\right)$

Thus, in the basis of its eigenvectors

$$\hat{U} = \begin{array}{cc}\begin{bmatrix}e^{-i\theta/4}&&&\\&e^{-i\theta/4}&&\\&&e^{+3i\theta/4}&\\&&&e^{-i\theta/4}\end{bmatrix} & \begin{array}{c}|\uparrow\uparrow\rangle\\|+\rangle\\|-\rangle\\|\downarrow\downarrow\rangle\end{array}\end{array}$$

Making the similarity transformation back to the standard bas

$$\hat{U} = \begin{bmatrix} 1 & & & \\ & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & \\ & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & \\ & & & 1 \end{bmatrix} \begin{bmatrix} e^{-i\theta/4} & & & \\ & e^{-i\theta/4} & & \\ & & e^{i3\theta/4} & \\ & & & e^{-i\theta/4} \end{bmatrix} \begin{bmatrix} 1 & & & \\ & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & \\ & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & \\ & & & 1 \end{bmatrix}$$

$$= \begin{array}{c} \left[\begin{array}{cccc} e^{-i\theta/4} & & & \\ & \frac{e^{\frac{-i\theta}{4}} + e^{\frac{i3\theta}{4}}}{2} & \frac{e^{\frac{-i\theta}{2}} - e^{\frac{i3\theta}{4}}}{2} & \\ & \frac{e^{\frac{-i\theta}{4}} - e^{\frac{i3\theta}{4}}}{2} & \frac{e^{\frac{-i\theta}{4}} + e^{\frac{i3\theta}{4}}}{2} & \\ & & & e^{-i\theta/4} \end{array}\right] \end{array} \begin{array}{c} |\uparrow\uparrow\rangle \\ |\uparrow\downarrow\rangle \\ |\downarrow\uparrow\rangle \\ |\downarrow\downarrow\rangle \end{array}$$

$$\Rightarrow \hat{U} = \begin{bmatrix} e^{-i\theta/4} & 0 & 0 & 0 \\ 0 & \multicolumn{2}{c}{\multirow{2}{*}{$e^{+i\theta/4}\begin{bmatrix} \cos\frac{\theta}{2} & -i\sin\frac{\theta}{2} \\ -i\sin\frac{\theta}{2} & \cos\frac{\theta}{2} \end{bmatrix}$}} & 0 \\ 0 & & & 0 \\ 0 & 0 & 0 & e^{-i\frac{\theta}{4}} \end{bmatrix}$$

where $\theta = Jt/\hbar$

(c) when $\theta = \pi$

$$\hat{U}(\pi) = e^{-i\pi/4} \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

With $|\psi_i\rangle = \alpha_i |\uparrow\rangle + \beta_i |\downarrow\rangle$

$$|\psi_A\rangle \otimes |\psi_B\rangle = \begin{bmatrix} \alpha_1 \alpha_2 \\ \alpha_1 \beta_2 \\ \beta_1 \alpha_2 \\ \beta_1 \beta_2 \end{bmatrix}$$ in the standard basis

$$\Rightarrow \hat{U}(\pi) \; |\psi_A\rangle \otimes |\psi_B\rangle = e^{-i\frac{\pi}{4}} \begin{bmatrix} \alpha_1 \alpha_2 \\ \beta_1 \alpha_2 \\ \alpha_1 \beta_2 \\ \beta_1 \beta_2 \end{bmatrix}$$

$$= e^{-i\pi/4} |\psi_B\rangle \otimes |\psi_A\rangle$$

Thus, the action of the interaction is to "swap" the states of the two spins

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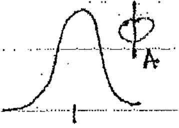
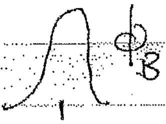
(d) The SWAP operation should not be confused with the "exchange" associated with Bose and Fermi symmetry.

The states we have been considering in this problem are spin states. In principle the state also contains a "motional" part, and for identical particles, we must symmetrize appropriately.

For example suppose the ~~case~~ spin state is an electron. Each electron is localized a separate position





$\phi_A(\vec{x})$ and $\phi_B(\vec{x})$ are localized wave packets

Suppose one electron is in spin state $|\chi_A\rangle$ if it is in wave pace ϕ_A and $|\chi_B\rangle$ if packet ϕ_B

Then, the total state is:

$$|\Psi(\vec{x}_1,\vec{x}_2)\rangle = \frac{1}{\sqrt{2}}\Big[\phi_A(\vec{x}_1)|\chi_A\rangle_1 \otimes \phi_B(\vec{x}_2)|\chi_B\rangle_2 - \phi_B(\vec{x}_1)|\chi_B\rangle_1 \otimes \phi_A(\vec{x}_2)|\chi_A\rangle_2\Big]$$

Here 1 and 2 lable electron #1 or #2. Of course we don't "know" which is which

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Now the *exchange* operators switches 1 and 2

$$\hat{P}_{exchange}|\Psi\rangle = \frac{1}{\sqrt{2}}\Big[\phi_A(\vec{x}_2)|\chi_A\rangle_2 \otimes \phi_B(\vec{x}_1)|\chi_B\rangle_1$$

$$- \phi_B(\vec{x}_2)|\chi_B\rangle_2 \otimes \phi_A(\vec{x}_1)|\chi_A\rangle_1\Big]$$

$$= -|\Psi\rangle$$ as expected for Fermions

In contrast

$$\hat{U}_{swa}|\Psi\rangle = \frac{1}{\sqrt{2}}\Big[\phi_A(\vec{x}_1)|\chi_B\rangle_1 \otimes \phi_B(\vec{x}_2)|\chi_A\rangle_2$$

$$- \phi_B(\vec{x}_1)|\chi_A\rangle_1 \otimes \phi_A(\vec{x}_2)|\chi_B\rangle_2\Big]$$

$$\neq \hat{P}_{exchange}|\Psi\rangle$$

In other words, the swap operation is switching the spin state of "that electron" which is localized in packet ϕ_A with the spin state of "that electron" in packet ϕ_B. The electron is essentially distinguished by its localized position.

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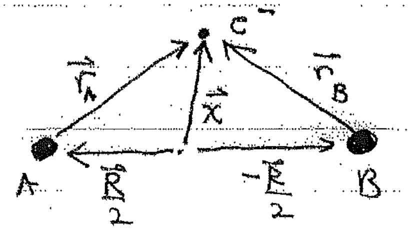
Problem 2: Diatomic Molecule

(a) H_2^+ molecule in the B-O approximation



- Two fixed protons.
- Electrons move very fast

$\Rightarrow$ Eigenstates parametrized by R

- Nuclei move slowly and electrons adiabatically follow

$$\hat{H} = \underbrace{\frac{\hat{p}^2}{2m} - \frac{e^2}{\hat{r}_A} - \frac{e^2}{\hat{r}_B}}_{\hat{H}'} + \underbrace{\frac{e^2}{R}}_{\text{Not operator}}$$

Trial ground-state wave function for electron

$$\tilde{\Psi}(\vec{x}) = c_A \psi_A(\vec{x}) + c_B \psi_B(\vec{x})$$

where $\psi_{A(B)}(\vec{x}) = \phi_{1S}\left(\vec{x} \mp \frac{\vec{R}}{2}\right) = \phi_{1S}(\vec{R}_{A(B)})$

with $\phi_{1S}(\vec{x}) = \frac{1}{\sqrt{\pi a_0^3}} e^{-\frac{|\vec{x}|}{a_0}}$ (The 1S Hydrogen orbital)

Variational energy

$$\bar{E}(c_A, c_B) = \frac{\langle\tilde{\Psi}|\hat{H}|\tilde{\Psi}\rangle}{\langle\tilde{\Psi}|\tilde{\Psi}\rangle}$$

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$$\langle\tilde{\psi}|\hat{H}|\tilde{\psi}\rangle = c_A^2\langle\psi_A|\hat{H}'|\psi_A\rangle + c_B^2\langle\psi_B|\hat{H}'|\psi_B\rangle$$

$$+ 2c_A c_B\langle\psi_B|\hat{H}'|\psi_A\rangle + \frac{e^2}{R}\langle\tilde{\psi}|\tilde{\psi}\rangle$$

(where I have used c_A, c_B real; $\psi_A(\vec{x}), \psi_B(\vec{x})$ real)

<u>Aside</u>: $\langle\psi_A|\hat{H}'|\psi_A\rangle = \langle\psi_A|\left(\frac{\hat{p}^2}{2m} - \frac{e^2}{\hat{r}_A}\right)|\psi_A\rangle + \langle\psi_A|\frac{-e^2}{\hat{r}_B}|\psi_A\rangle$

$$\langle\psi_B|\hat{H}'|\psi_B\rangle = \langle\psi_B|(\frac{\hat{p}^2}{2m} - \frac{e^2}{\hat{r}_B}|\psi_B\rangle + \langle\psi_B|-\frac{e^2}{\hat{r}_A}|\psi_B\rangle$$

Using the symmetry of the problem, we see that

- $\langle\psi_A|\frac{\hat{p}^2}{2m} - \frac{e^2}{\hat{r}_A}|\psi_A\rangle = \langle\psi_B|\frac{\hat{p}^2}{2m} - \frac{e^2}{\hat{r}_A}|\psi_B\rangle = E_H^{(1s)} \simeq -13.6\,\text{eV}$
- $\langle\psi_A|-\frac{e^2}{\hat{r}_B}|\psi_A\rangle = \langle\psi_B|-\frac{e^2}{\hat{r}_A}|\psi_B\rangle \equiv I$ ("Coulomb integral")

(Given $I = \int d^3x\,|\psi_A(\vec{x})|^2\left(\frac{-e^2}{r_B}\right) = \frac{e^2}{a_0}\left(-\frac{1}{\bar{R}} + e^{-2\bar{R}}\left(1+\frac{1}{\bar{R}}\right)\right)$

$(\bar{R} \equiv R/a_0)$

<u>Aside</u>: $\langle\psi_B|\hat{H}'|\psi_A\rangle = \underbrace{\langle\psi_B|\left(\frac{\hat{p}^2}{2m} - \frac{e^2}{\hat{r}_A}\right)|\psi_A\rangle}_{\text{Eigenstate } E_H^{(1s)}|\psi_A\rangle} + \langle\psi_B|\frac{-e^2}{\hat{r}_B}|\psi_A\rangle$

$$= E_H^{(1s)} P_{AB} + M$$

where $P_{AB} = \langle\psi_B|\psi_A\rangle = e^{-\bar{R}}\left(1 + \bar{R} + \frac{\bar{R}^2}{3}\right)$

$$M = \langle\psi_B|-\frac{e^2}{\hat{r}_B}|\psi_A\rangle = \int d^3x\,\psi_B(\vec{x})\left(\frac{-e}{r_B}\right)\psi_A(\vec{x})$$

$$= -\frac{e^2}{a_0}e^{-\bar{R}}(1+\bar{R})$$ ("Resonance integral")

Finally $\langle\tilde{\Psi}|\tilde{\Psi}\rangle = c_A^2 + c_B^2 + 2c_{AB}P_{AB}$

thus the variational energy is

$$\bar{E}(c_A, c_B) = \frac{\left(E_H^{(1s)}(c_A^2+c_B^2+2c_{AB}P_{AB}) + (c_A^2+c_B^2)I + 2c_Ac_B M\right) + \frac{e^2}{R}\langle\tilde{\Psi}|\tilde{\Psi}\rangle)}{c_A^2+c_B^2+2c_Ac_BP_{AB}}$$

$$\Rightarrow \boxed{\bar{E}(c_A, c_B) = E_H(1s) + \frac{(c_A^2+c_B^2)I + 2c_Ac_BM}{c_A^2+c_B^2+2c_Ac_BP_{AB}} + \frac{e^2}{R}}$$

Now we must minimized w.r.t. the parameters c_A and c_B. We seek the solutions to

$$\frac{\partial\bar{E}}{\partial c_A} = \frac{\partial\bar{E}}{\partial c_B} = 0$$

After some algebra:

$$\Rightarrow \frac{2c_B(c_A^2-c_B^2)(IP_{AB}-M)}{(c_A^2+c_B^2+2c_Ac_BP_{AB})^2} = 0 = \frac{-2c_A(c_A^2-c_B^2)(IP_{AB}-M)}{(c_A^2+c_B^2+2c_Ac_BP_{AB})^2}$$

Since $I<0$ $M<0$ $P_{AB}>0$ ~~and both c_A and $c_B \neq 0$~~

$$\Rightarrow c_A^2 - c_B^2 = 0$$

$$\Rightarrow \boxed{c_A = \pm c_B}$$ To minimize ~~gr~~ energy

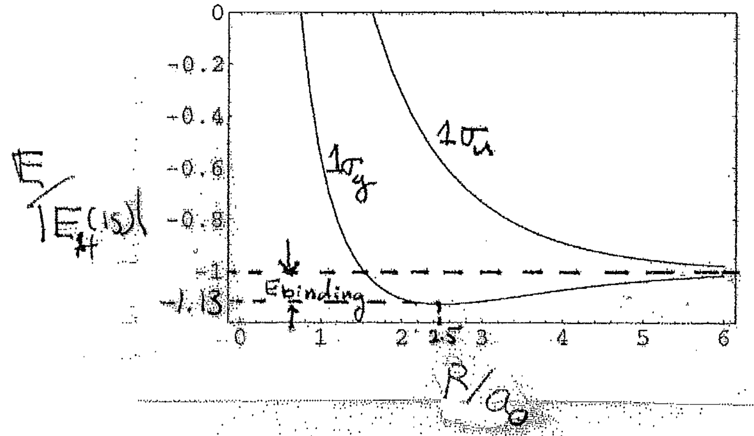
Thus, the variational solution for the ground state energy involve symmetric and antisymmetric combinations of the atomic orbitals (as we could have guessed): these correspond to the "gerade" and "ungerade" solutions for the electron parity:

$$\boxed{\begin{aligned} |1\sigma_{g(u)}\rangle &= |\psi_A\rangle \pm |\psi_B\rangle \qquad \text{(unnormalized)} \\ E(1\sigma_{g(u)}) &= E_H(1s) + \frac{I \pm M}{1 \pm P_{AB}} + \frac{e^2}{R} \end{aligned}}$$

Here the electron wave function is denoted as a "molecular orbital" $|l_z|_p \leftarrow$ parity $(\sigma \to l_z = 0)$

$\uparrow$ angular momentum about internuclear axis

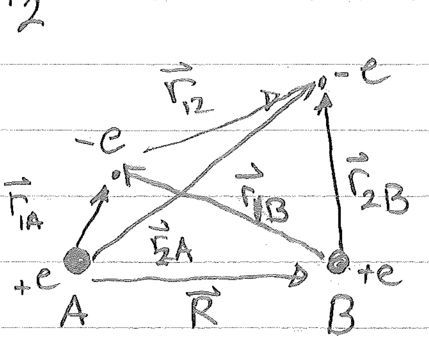
(b) Plugging in the R dependence for the Coulomb and resonance integral we arrive at the B-O potential for the nuclei.



We see that the $1\sigma_g$ state provides a shallow binding potential for the nuclei

- Equilbrium separation $2.5\,a_0$
- Binding energy $0.13\,|E_H(1s)| \simeq 1.76\,eV$

(c) Neutral H_2 molecule in the Born-Oppenheimer Approx.



Two electron and Two protons. Protons are fixed in position as electrons move. $\vec{R}$ is a classical variable

$$\hat{H} = \underbrace{\frac{\vec{P}_1^{\,2}}{2m} + \frac{\vec{P}_2^{\,2}}{2m}}_{\text{electron kinetic energy}} \underbrace{- \frac{e^2}{r_{1A}} - \frac{e^2}{r_{2A}} - \frac{e^2}{r_{1B}} - \frac{e^2}{r_{2B}}}_{\text{electron-proton attraction}} + \underbrace{\frac{e^2}{r_{12}}}_{\text{electron-electron repulsion}} + \underbrace{\frac{e^2}{R}}_{\text{proton-proton repulsion}}$$

In the Heitler-London model, we think of the molecule as forming from two neutral atoms. Thus, we take as our trial wavefunction

$$\tilde{\Psi}(\vec{x}_1, \vec{x}_2) = \underbrace{c\, \psi_A(\vec{x}_1)\, \psi_B(\vec{x}_2)}_{\substack{\text{electron 1 in orbital A} \\ \text{2 " " B}}} + d\, \underbrace{\psi_B(\vec{x}_1)\, \psi_A(\vec{x}_2)}_{\substack{\text{electron 1 in orbital B} \\ \text{2 " " A}}}$$

We can, for example, think of this as one electron in the 1s orbital localized at proton A and the other in the 1s orbital localized at proton B. This should be a good approximation to the molecule close to dissociation

To facilitate the calculation, I will use Dirac notation

trial state: $|\tilde{\Psi}\rangle = c\,|\psi_A\rangle|\psi_B\rangle + d\,|\psi_B\rangle|\psi_A\rangle$

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_{12}$$

$$\hat{H}_1 = \frac{\hat{p}_1^{\,2}}{2m} - \frac{e^2}{\hat{r}_{1A}} - \frac{e^2}{\hat{r}_{1B}} = \underset{\substack{\Uparrow \\ \text{Hydrogen} \\ \text{atom at A}}}{\hat{H}_{1A}} - \frac{e^2}{\hat{r}_{1B}} = \underset{\substack{\Uparrow \\ \text{Hydrogen} \\ \text{atom at B}}}{\hat{H}_{1B}} - \frac{e^2}{\hat{r}_{1A}}$$

$$\hat{H}_2 = \hat{H}_{2A} - \frac{e^2}{\hat{r}_{2B}} = \hat{H}_{2B} - \frac{e^2}{\hat{r}_{2A}}$$

$$\hat{H}_{12} = \frac{e^2}{\hat{r}_{12}}$$

<u>A side:</u>

$$\hat{H}_1|\tilde{\Psi}\rangle = c\left(\hat{H}_{1A} - \frac{e^2}{\hat{r}_{1B}}\right)|\psi_A\rangle \otimes |\psi_B\rangle + d\left(\hat{H}_{1B} - \frac{e^2}{\hat{r}_{1A}}\right)|\psi_B\rangle \otimes |\psi_A\rangle$$

$$= E_H(1s)|\tilde{\Psi}\rangle + \Big[c\left(-\frac{e^2}{r_{1B}}\right)|\psi_A\rangle|\psi_B\rangle + d\left(-\frac{e^2}{r_{1A}}\right)|\psi_B\rangle|\psi_A\rangle\Big)$$

$$\Rightarrow \langle\tilde{\Psi}|\hat{H}_1|\tilde{\Psi}\rangle = E_H(1s)\langle\tilde{\Psi}|\tilde{\Psi}\rangle + (c^2+d^2)\,I + 2cd\,M\,P_{AB}$$

$$= \langle\tilde{\Psi}|\hat{H}_2|\tilde{\Psi}\rangle$$

where I, M, P_{AB} are defined in part (a)

The interaction term is as in Helium:

$$\langle\tilde{\Psi}|\frac{e^2}{r_{12}}|\tilde{\Psi}\rangle = (c^2+d^2)\,K + 2cd\,J$$

where $K = \int d^3x_1\, d^3x_2\, \psi_A^2(\vec{x}_1)\, \psi_B(\vec{x}_2)\, \frac{e^2}{r_{12}}$ (Direct term)

$$J = \int d^3x_1\, d^3x_2\, \psi_A(\vec{x}_1)\psi_B(\vec{x}_2)\,\frac{e^2}{r_{12}}\,\psi_B(\vec{x}_1)\psi_A(\vec{x}_2)$$

(exchangeterm)

$\Longrightarrow$ Variational energy

$$\bar{E}(c,d) = \frac{\langle\tilde{\Psi}|\hat{H}|\tilde{\Psi}\rangle}{\langle\tilde{\Psi}|\tilde{\Psi}\rangle} = \frac{\langle\tilde{\Psi}|\hat{H}|\tilde{\Psi}\rangle}{c^2+d^2+2cd\,P_{AB}^2} + \frac{e^2}{R}$$

$$= 2E_H(1s) + \frac{(c^2+d^2)(2I+K) + 2cd(2MP_{AB}+J)}{c^2+d^2+2cd\,P_{AB}^2} + \frac{e^2}{R}$$

Minimize $\frac{\partial\bar{E}}{\partial c} = \frac{\partial\bar{E}}{\partial d} = 0 \Rightarrow c = \pm d$

$\Longrightarrow$ Heitler-London ground states

$$\boxed{E(1\Sigma_{g,u}) = 2E_H(1s) + \frac{2I+K \pm (2MP_{AB}+J)}{1 \pm P_{AB}^2} + \frac{e^2}{R}}$$

where $|\tilde{\Psi}\rangle = |\psi_A\rangle|\psi_B\rangle \pm |\psi_B\rangle|\psi_A\rangle$

(unnormalized)

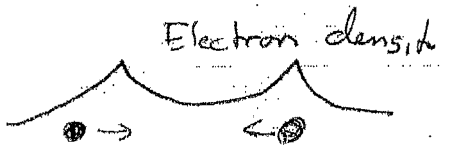
(e) the Pauli principle insists of complete antisymmetry. Thus we must have

$$|{}^1\Sigma_g\rangle = \underbrace{|\Sigma_g\rangle}_{\substack{\text{symmetric}\\ \text{spatial}}} \otimes \underbrace{|\chi_s\rangle}_{\substack{\text{singlet}\\ \text{anti-sym spin}}}$$

or

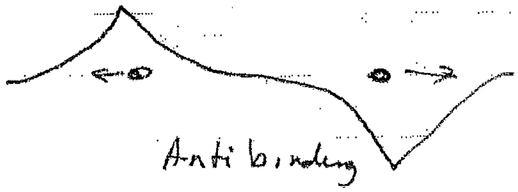
$$|{}^3\Sigma_u\rangle = \underbrace{|\Sigma_u\rangle}_{\substack{\text{anti}\\ \text{symmetric}\\ \text{spatial}}} \otimes \underbrace{|\chi_T\rangle}_{\substack{\text{triplet}\\ \text{symmetric-spin}}}$$

The singlet, being symmetric spatially is binding. this makes sense physically since the symmetric state will have more of the electron charge at the origin between the nuclei, providing an attractive force. the triplet will have an anti-symmetric spatial wavefunction, providing repulsion:



Binding

$^1\Sigma_g$



Antibinding

$^3\Sigma_u$

A copy of the H_2 B-O potentials is shown below:

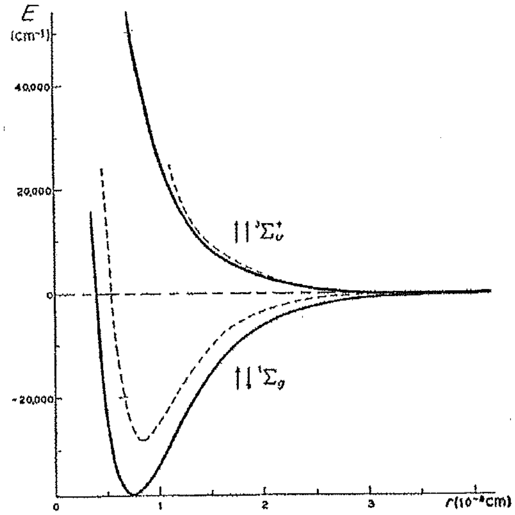


Fig. 161. **Potential Curves of the Two Lowest States of the H_2 Molecule.** The full line curves are the final curves resulting from the calculations of James and Coolidge (361)(859), which agree with the observed data; the broken line curves are first approximations as given by Heitler (1024a) (see p. 353 f.).

From Herzberg "Spectra of Diatomic Molecules", Van Nortrand Reinhold, 1950