Problem Set 13
On molecular orbitals of diatomic molecules and the Pauli exclusion principle

1. To describe the electronic structure of atoms having more than one electron, we first start out by solving the hydrogen-like atom; that is, we first solved the system having only one electron and found the eigenfunctions and the eigenvalues in terms of the charge on the nucleus, +Ze. The eigenfunctions we found are $R_{n\ell}(Z, r) \bullet Y_{\ell m}(\theta, \phi)$,
and the eigenvalues $E_n = -(Z/n)^2 (e^2/2a)$.
Then to describe the electronic structure of atoms having more than one electron we considered a model such as the central field approximation that permits us to consider one electron at a time, that is, the central field approximation Hamiltonian looks like

$$\mathcal{H} = \sum_i \{ -(\hbar^2/2\mu)\nabla_i^2 + V(r_i) \}$$

In using the central field approximation, we find that the Schrödinger equation for the electronic motion is separable; i.e., we only need to solve the problem of one electron at a time and find functions of the coordinates of one electron only (so-called ‘orbitals’ or ‘atomic orbitals’ since these are for an atom):
Solving the equation,
$\{ -(\hbar^2/2\mu)\nabla_3^2 + V(r_3) \}\Psi(r_3, \theta_3, \phi_3) = \varepsilon_3 \Psi(r_3, \theta_3, \phi_3)$ for electron 3 for example,
leads to the functions $\Psi(r_3, \theta_3, \phi_3) = F(r_3)\bullet Y_{\ell m}(\theta_3, \phi_3)$.
When the Slater approximation is also used, then
$F(r_3)$ takes the form of $R_{n\ell}(Z_{\text{eff},3}, r_3)$ and ε_3 takes the form of $-(Z_{\text{eff},3}/n)^2 (e^2/2a_0)$, the solutions to the hydrogen-like atom with $+Z_{\text{eff}}\,e$ as the nuclear charge.

Now, for electronic motion in the H_2 diatomic molecule, we do something analogous. We consider the simplest diatomic molecule with only one electron, the H_2^+ molecule ion.

$$\mathcal{H}_{\text{elec}} = \{ -(\hbar^2/2m)\nabla^2 + V(\mathbf{r}) \}$$

where $V(\mathbf{r})$ includes attraction to both nuclear charges $+Z_A e$ and $+Z_B e$ and is a function of the position coordinates of the electron in the axis frame formed by the nuclei.
The $(+Z_A e)(+Z_B e)/R_{AB}$ is a constant contribution to the potential energy for each internuclear distance, and can simply be added to the electronic energy eigenvalue found at each R_{AB} .

We assume that we have found all the electronic eigenfunctions for the H_2^+ molecule ion, and these one-electron functions are called ‘molecular orbitals’. Next we consider the <u>two-electron</u> diatomic molecule by thinking in terms of absorbing the electronic repulsion hamiltonian term $+e^2/r_{12}$ partly into $V(\mathbf{r}_1)$ and the rest into $V(\mathbf{r}_2)$, where the bold $\mathbf{r}_1$ stands for the position coordinates of electron 1 in the nuclear frame of the molecule and of course $V(\mathbf{r}_1)$ includes attraction to both nuclear charges $+Z_{A,\text{eff}}e$ and $+Z_{B,\text{eff}}e$. If we do this, then our Hamiltonian for electronic motion becomes

$$\mathcal{H}_{\text{elec}} = \sum_{i=1,2} \{ -(\hbar^2/2m)\nabla_i^2 + V(r_i) \}$$

and, just as in the case of the many-electron atoms, we end up by using separation of variables, therefore our electronic eigenfunctions of energy will be expressible in terms of products like $\psi(\mathbf{r}_1)\bullet\psi(\mathbf{r}_2)$ where $\psi(\mathbf{r}_1)$ is a one-electron function, therefore called a 'molecular orbital' since the electronic coordinate ($\mathbf{r}_1$) describes its position in the frame of the several nuclei in the molecule (here only two, nucleus A and nucleus B). The H_2 molecule is simple enough that we can examine the Pauli exclusion principle at work. This is what the following question is about.

Let us write the lowest energy electronic eigenfunction of the H_2^+ molecule ion in the simplest possible MO (molecular orbital) approximation:

$\psi(\mathbf{r}_1) = \sigma_g\,(1) = [2 + 2S]^{½}\,[\phi_A(1) + \phi_B(1)]$, ϕ_A is a 1s atomic orbital centered on nucleus A, S is an overlap integral

Another eigenfunction of the H_2^+ molecule ion, again in the simplest possible MO approximation is

$\psi(\mathbf{r}_1) = \sigma_u\,(1) = [2 - 2S]^{½}\,[\phi_A(1) - \phi_B(1)]$.

If we use only the above one-electron functions (MOs), there are four spin-orbitals which are possible for one electron:

$\sigma_g(1)\bullet\alpha(1)$ $\sigma_g(1)\bullet\beta(1)$ $\sigma_u(1)\bullet\alpha(1)$ $\sigma_u(1)\bullet\beta(1)$

Now to build a description of H_2 molecule. There are 2 electrons and from the above molecular orbitals we have the possible combinations:

any of	$\sigma_g(1)\bullet\alpha(1)$	$\sigma_g(1)\bullet\beta(1)$	$\sigma_u(1)\bullet\alpha(1)$	$\sigma_u(1)\bullet\beta(1)$
with any of	$\sigma_g(2)\bullet\alpha(2)$	$\sigma_g(2)\bullet\beta(2)$	$\sigma_u(2)\bullet\alpha(2)$	$\sigma_u(2)\bullet\beta(2)$

	space part	spin part
1	$\sigma_g(1)\bullet\sigma_g(2)$	$\alpha(1)\bullet\alpha(2)$
2	$\sigma_g(1)\bullet\sigma_g(2)$	$\alpha(1)\bullet\beta(2)$
3	$\sigma_g(1)\bullet\sigma_u(2)$	$\alpha(1)\bullet\alpha(2)$
4	$\sigma_g(1)\bullet\sigma_u(2)$	$\alpha(1)\bullet\beta(2)$
5	$\sigma_g(1)\bullet\sigma_g(2)$	$\beta(1)\bullet\alpha(2)$
6	$\sigma_g(1)\bullet\sigma_g(2)$	$\beta(1)\bullet\beta(2)$
7	$\sigma_g(1)\bullet\sigma_u(2)$	$\beta(1)\bullet\alpha(2)$
8	$\sigma_g(1)\bullet\sigma_u(2)$	$\beta(1)\bullet\beta(2)$

	space part	spin part
9	$\sigma_u(1)\bullet\sigma_g(2)$	$\alpha(1)\bullet\alpha(2)$
10	$\sigma_u(1)\bullet\sigma_g(2)$	$\alpha(1)\bullet\beta(2)$
11	$\sigma_u(1)\bullet\sigma_u(2)$	$\alpha(1)\bullet\alpha(2)$
12	$\sigma_u(1)\bullet\sigma_u(2)$	$\alpha(1)\bullet\beta(2)$
13	$\sigma_u(1)\bullet\sigma_g(2)$	$\beta(1)\bullet\alpha(2)$
14	$\sigma_u(1)\bullet\sigma_g(2)$	$\beta(1)\bullet\beta(2)$
15	$\sigma_u(1)\bullet\sigma_u(2)$	$\beta(1)\bullet\alpha(2)$
16	$\sigma_u(1)\bullet\sigma_u(2)$	$\beta(1)\bullet\beta(2)$

However, we can not use these spin functions as is because they are eigenfunctions of S_z , but are not all eigenfunctions of S^2 .

We can form the eigenfunctions of S^2 from the above spin functions that are already eigenfunctions of S_z.

Eigenfunctions of S_z	M_S
$\alpha(1)\bullet\alpha(2)$	$+½ + ½ = 1$

S	Eigenfunctions of S^2
1	$\alpha(1)\bullet\alpha(2)$

$\beta(1)\bullet\beta(2)$	$-\frac{1}{2} - \frac{1}{2} = -1$		1	$\beta(1)\bullet\beta(2)$
$\alpha(1)\bullet\beta(2)$	$+\frac{1}{2} - \frac{1}{2} = 0$	degenerate	1	$1/\sqrt{2}\{\alpha(1)\bullet\beta(2)+ \beta(1)\bullet\alpha(2)\}$
$\beta(1)\bullet\alpha(2)$	$-\frac{1}{2} + \frac{1}{2} = 0$	degenerate	0	$1/\sqrt{2}\{\alpha(1)\bullet\beta(2)- \beta(1)\bullet\alpha(2)\}$

(a) Question: *Classify each of the above 4 functions that are eigenfunctions of S^2 according to 'symmetric' or 'antisymmetric' with respect to interchange of electrons 1 and 2.*

Similarly, since electron 1 and 2 are indistinguishable, we can form linear combinations of the space part when only the labels 1 and 2 distinguish the product functions

Eigenfunctions of $\mathcal{H}$ $\mathcal{H}(1) + \mathcal{H}(2)$: $\psi(\mathbf{r}_1) \bullet \psi(\mathbf{r}_2)$			Eigenfunctions of $\mathcal{H}(1) + \mathcal{H}(2)$
$\sigma_g(1)\bullet\sigma_g(2)$	$2E\sigma_g$		$\sigma_g(1) \bullet\sigma_g(2)$
$\sigma_u(1)\bullet\sigma_u(2)$	$2E\sigma_u$		$\sigma_u(1) \bullet\sigma_u(2)$
$\sigma_g(1)\bullet\sigma_u(2)$	$E\sigma_g + E\sigma_u$	degenerate	$1/\sqrt{2}\{\sigma_g(1)\bullet\sigma_u(2) +\sigma_u(1)\bullet\sigma_g(2)\}$
$\sigma_u(1)\bullet\sigma_g(2)$	$E\sigma_g + E\sigma_u$	degenerate	$1/\sqrt{2}\{\sigma_g(1)\bullet\sigma_u(2) - \sigma_u(1)\bullet\sigma_g(2)\}$

(b) Question: *Classify each of the above 4 functions that are eigenfunctions of $\mathcal{H}$ according to 'symmetric' or 'antisymmetric' with respect to interchange of electrons 1 and 2.*

We still have 4space x 4spin = 16 functions that we can use, just as before we made the linear combinations.

(c) Question: *Determine which combinations are allowed by the Pauli exclusion principle [The total wavefunction has to be 'antisymmetric' (must change sign) with respect to interchange of any two electrons (fermions).]*

Now, let us write out the functions in terms of the atomic orbitals within the MOs:

$\sigma_g(1) = [2 + 2S]^{\frac{1}{2}} [\phi_A(1) + \phi_B(1)]$ and $\sigma_u(1) = [2 - 2S]^{\frac{1}{2}} [\phi_A(1) - \phi_B(1)]$

Eigenfunctions of $\mathcal{H}(1) + \mathcal{H}(2)$:		
$\sigma_g(1)\bullet\sigma_g(2)$	$[2 + 2S] [\phi_A(1)\bullet\phi_B(2) + \phi_B(1)\bullet\phi_A(2) + \phi_A(1)\bullet\phi_A(2) + \phi_B(1)\bullet\phi_B(2)]$	$2E\sigma_g$
$\sigma_u(1)\bullet\sigma_u(2)$	$[2 + 2S] [-\phi_A(1)\bullet\phi_B(2) - \phi_B(1)\bullet\phi_A(2) + \phi_A(1)\bullet\phi_A(2) + \phi_B(1)\bullet\phi_B(2)]$	$2E\sigma_u$
$1/\sqrt{2}\{\sigma_g(1)\bullet\sigma_u(2) - \sigma_u(1)\bullet\sigma_g(2)\}$	$[2(1-S^2)]^{\frac{1}{2}} [-\phi_A(1)\bullet\phi_B(2) + \phi_B(1)\bullet\phi_A(2)]$	$E\sigma_g + E\sigma_u$
$1/\sqrt{2}\{\sigma_g(1)\bullet\sigma_u(2) + \sigma_u(1)\bullet\sigma_g(2)\}$	$[2(1-S^2)]^{\frac{1}{2}} [\phi_A(1)\bullet\phi_A(2) - \phi_B(1)\bullet\phi_B(2)]$	$E\sigma_g + E\sigma_u$

(d) Question: *Classify each of the above 4 functions that are eigenfunctions of $\mathcal{H}$ according to 'symmetric' or 'antisymmetric' with respect to interchange of protons A and B.*

Now consider the nuclear spin of nuclei A and B, the two protons. The proton has spin I=½ . We can form the eigenfunctions of square of nuclear spin angular momentum $\boldsymbol{I}^2$ from the above spin functions that are already eigenfunctions of $\boldsymbol{I}_z$.

Eigenfunctions of $\boldsymbol{I}_z$	M_I	
$\alpha(A)\bullet\alpha(B)$	+½ + ½ = 1	
$\beta(A)\bullet\beta(B)$	-½ - ½ = -1	
$\alpha(A)\bullet\beta(B)$	+½ - ½ = 0	degenerate
$\beta(A)\bullet\alpha(B)$	-½ + ½ = 0	degenerate

I	Eigenfunctions of $\boldsymbol{I}^2$
1	$\alpha(A)\bullet\alpha(B)$
1	$\beta(A)\bullet\beta(B)$
1	$1/\sqrt{2}\{\alpha(A)\bullet\beta(B)+\beta(A)\bullet\alpha(B)\}$
0	$1/\sqrt{2}\{\alpha(A)\bullet\beta(B)-\beta(A)\bullet\alpha(B)\}$

(e) Question: *Classify the above 4 functions that are eigenfunctions of* $\boldsymbol{I}^2$ *according to 'symmetric' or 'antisymmetric' with respect to interchange of protons A and B.*

Of course to have the total wavefunction of a diatomic molecule we still have to multiply the functions that we have considered above by the missing parts of the wavefunction, i.e., translation, vibration, and rotation. Assume that the vibrational part of the wavefunction can be approximated by a harmonic oscillator function. (See your text book for these functions.) These functions do not change when nuclei A and B are interchanged since the harmonic oscillator functions depend only on displacements from the equilibrium (minimum energy geometry) distance R_{AB}.
We already derived the translational wavefunctions of any molecule, these are the functions of a particle in a three-dimensional box of dimensions L_1, L_2, L_3. These functions do not change when nuclei A and B are interchanged.
We already derived the rotational wavefunctions for a rigid rotor. We can approximate the rotational wavefunctions of a diatomic molecule with those of a rigid rotor; they are the same mathematical form as the energy eigenfunctions of a particle on the surface of a sphere: $Y_{J,M}(\theta,\phi)$. Interchanging nuclei A and B in a rigid rotor (when A and B ends are indistinguishable, i.e., same mass) is the same as inverting the two masses through the center of mass of the molecule, the result of which depends on the θ part as follows:

$$P_{AB}\, Y_{J,M}(\theta,\phi) = (-1)^J Y_{J,M}(\theta,\phi)$$

(f) Now put <u>all</u> the functions together, *write <u>the total wavefunction</u> of* H_2 *molecule, including everything. Determine which of the above 4 nuclear spin functions may be used with your set of all other functions so that the total wavefunction of* H_2 *molecule obeys the Pauli exclusion principle with respect to interchange of the two indistinguishable protons A and B.*
You may express your wavefunction in terms of the usual variables and constants for the H_2 molecule, but define the symbols you use.
(g) Consider the rotational energies of the H_2 molecule. For the ground electronic state and ground vibrational state of the H_2 molecule, *calculate the rotational energy in terms of* $(\hbar^2/2\mu R_{AB}^2)$*, up to rotational quantum number J = 4*. For up to J = 4, *write the total energy* of the H_2 molecule (in addition to translational energy) and *write an*

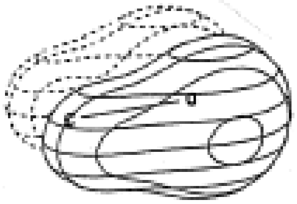
expression for the total wavefunction for each of the two lowest J. For up to J = 4, in the ground electronic and ground vibrational state of H_2 molecule, calculate the number of degenerate states (including electron spins, nuclear spins, electronic and vibrational states) that have the same energy. *Draw the rotational energy level diagram* to scale, up to J = 4. To each energy level *attach the labels*: J, the total degeneracy, and the rotational energy.

(h) Now consider the heavy hydrogen molecule D_2. The deuteron has spin I = 1. Look carefully at the constants and functions that you have written down in the above H_2 molecule case and *identify every part that will become different upon going from H_2 to D_2 .* [Hint: Look everywhere there are masses and spins I that are involved, and follow through for the D_2 molecule the same arguments as are shown in part (e) above for the H_2 molecule.] *Prepare a table for D_2 as shown in part (e) for H_2.*

(i) and (j) *Demonstrate that you understand the differences by writing out the D_2 case just as you did the H_2 case in parts (f) and (g).*

2. *Assign the appropriate molecular orbital designation* [σ, π, δ, ..., u or g, bonding or anti-bonding (*), atomic orbital composition] *to each of the following one-electron functions.* For consistency of notation, designate the plane of the paper as the xz plane. The identity of the atoms are indicated by the symbols at the nuclei.

(a)



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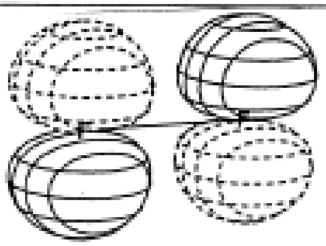

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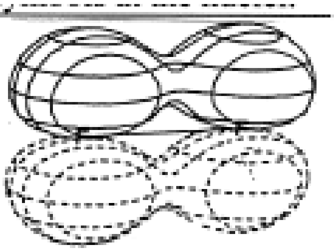

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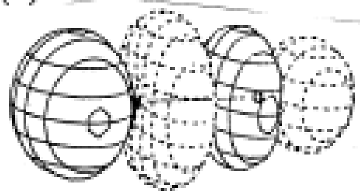

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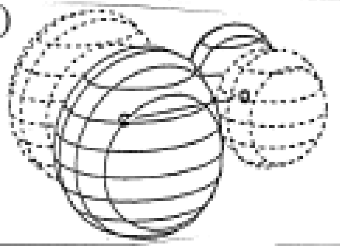

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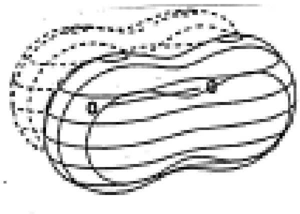

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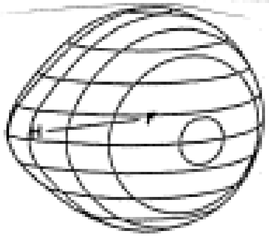

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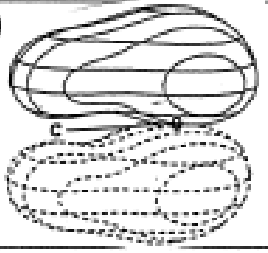
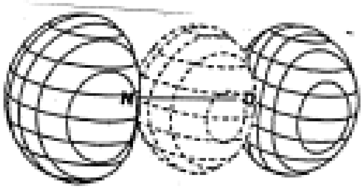


(i)



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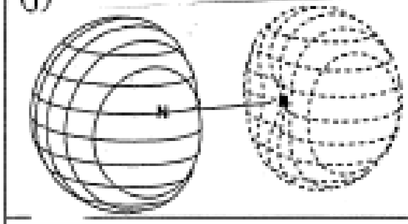

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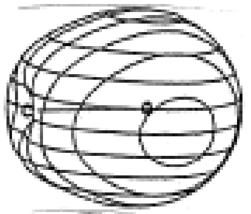

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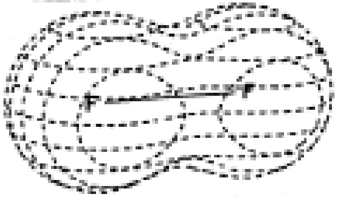

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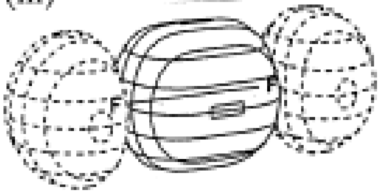

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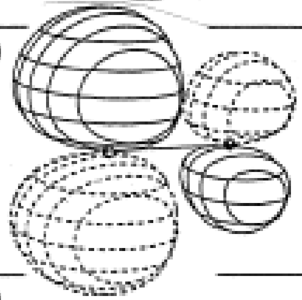

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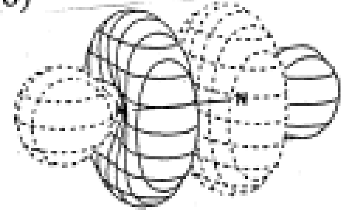

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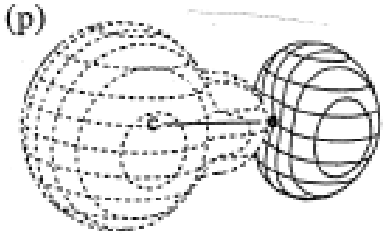

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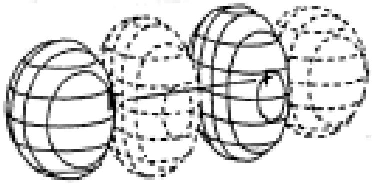

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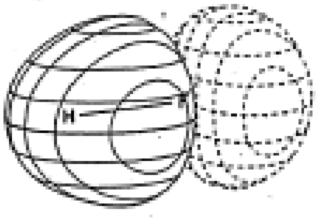
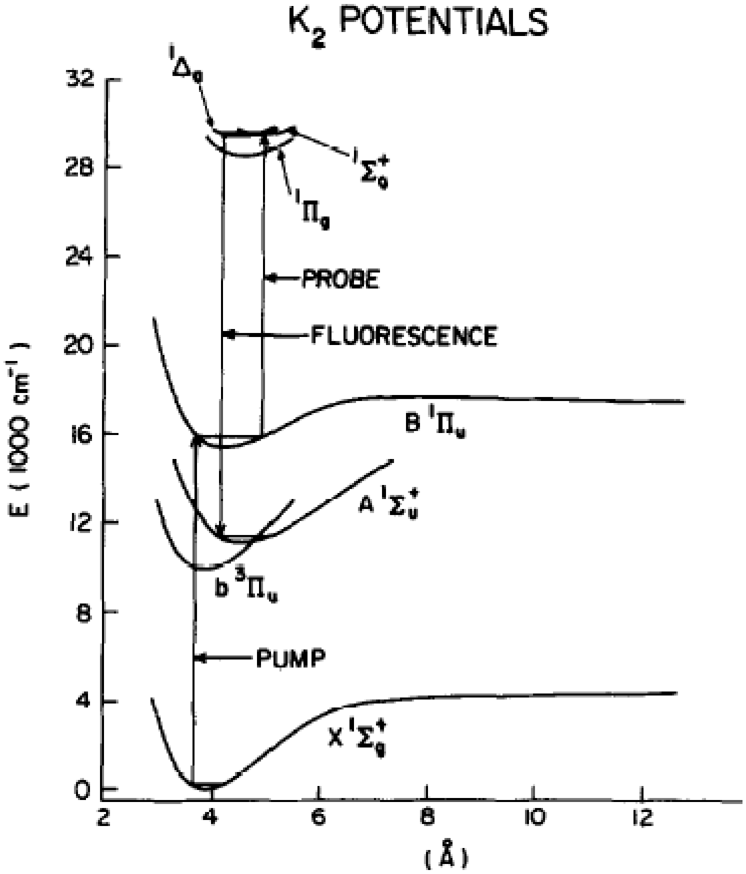


3. The K_2 potential functions are shown in the figure below. The labels correspond to the electronic states of the 38-electron diatomic molecule. If, subsequent to the Born-Oppenheimer separation, these 38 electrons were to be considered as describable by an antisymmetrized product of 38 one-electron functions, which product function approximately describes the ground state? In other words, *what is a likely "electronic configuration" in terms of molecular orbitals* for the electronic ground state of K_2 molecule? Provide electronic configurations *for* as many as you can of *the excited electronic states* as well.



H. Wang, L. Li, A.M. Lyyra and W.C. Stwalley, *J. Mol. Spectrosc.* **137** (1989), p. 304.