Problem Set 13 answers

1.

$P_{12}\, \Psi_{elec\ space}(1,2)$:

$P_{12}\sigma_g(1)\bullet\sigma_g(2) = +\ \sigma_g(1)\bullet\sigma_g(2)$

$P_{12}\sigma_u(1)\bullet\sigma_u(2) = +\ \sigma_u(1)\bullet\sigma_u(2)$

$P_{12}\ 1/\sqrt{2}\{\sigma_g(1)\bullet\sigma_u(2) + \sigma_u(1)\bullet\sigma_g(2)\} = +\ 1/\sqrt{2}\{\sigma_g(1)\bullet\sigma_u(2) + \sigma_u(1)\bullet\sigma_g(2)\}$

$P_{12}\ 1/\sqrt{2}\{\sigma_g(1)\bullet\sigma_u(2) - \sigma_u(1)\bullet\sigma_g(2)\} = -\ 1/\sqrt{2}\{\sigma_g(1)\bullet\sigma_u(2) - \sigma_u(1)\bullet\sigma_g(2)\}$

$P_{12}\, \Psi_{elec\ spin}(1,2)$:

$P_{12}\ \alpha(1)\bullet\alpha(2) = +\ \alpha(1)\bullet\alpha(2)$

$P_{12}\ \beta(1)\bullet\beta(2) = +\ \beta(1)\bullet\beta(2)$

$P_{12}\ 1/\sqrt{2}\{\alpha(1)\bullet\beta(2)+ \beta(1)\bullet\alpha(2)\} = +\ 1/\sqrt{2}\{\alpha(1)\bullet\beta(2)+ \beta(1)\bullet\alpha(2)\}$

$P_{12}\ 1/\sqrt{2}\{\alpha(1)\bullet\beta(2)- \beta(1)\bullet\alpha(2)\} = -\ 1/\sqrt{2}\{\alpha(1)\bullet\beta(2)- \beta(1)\bullet\alpha(2)\}$

$P_{AB}\Psi_{elec\ space}(1,2)$:

$P_{AB}\sigma_g(1)\bullet\sigma_g(2) = P_{AB}\ [2 + 2S]\ [\phi_A(1)\bullet\phi_B(2) + \phi_B(1)\bullet\phi_A(2) + \phi_A(1)\bullet\phi_A(2) + \phi_B(1)\bullet\phi_B(2)]$

$= +\ [2 + 2S]\ [\phi_A(1)\bullet\phi_B(2) + \phi_B(1)\bullet\phi_A(2) + \phi_A(1)\bullet\phi_A(2) + \phi_B(1)\bullet\phi_B(2)]$

$P_{AB}\sigma_u(1)\bullet\sigma_u(2) = P_{AB}[2 + 2S]\ [-\phi_A(1)\bullet\phi_B(2) - \phi_B(1)\bullet\phi_A(2) + \phi_A(1)\bullet\phi_A(2) + \phi_B(1)\bullet\phi_B(2)]$

$= +\ [2 + 2S]\ [-\phi_A(1)\bullet\phi_B(2) - \phi_B(1)\bullet\phi_A(2) + \phi_A(1)\bullet\phi_A(2) + \phi_B(1)\bullet\phi_B(2)]$

$P_{AB}\ 1/\sqrt{2}\{\sigma_g(1)\bullet\sigma_u(2) - \sigma_u(1)\bullet\sigma_g(2)\} = P_{AB}[2(1-S^2)]^{1/2}\ [-\phi_A(1)\bullet\phi_B(2) + \phi_B(1)\bullet\phi_A(2)]$

$= -\ [2(1-S^2)]^{1/2}\ [-\phi_A(1)\bullet\phi_B(2) + \phi_B(1)\bullet\phi_A(2)]$

$P_{AB}\ 1/\sqrt{2}\{\sigma_g(1)\bullet\sigma_u(2) + \sigma_u(1)\bullet\sigma_g(2)\} = P_{AB}[2(1-S^2)]^{1/2}\ [\ \phi_A(1)\bullet\phi_A(2) - \phi_B(1)\bullet\phi_B(2)]$

$= -\ [2(1-S^2)]^{1/2}\ [\ \phi_A(1)\bullet\phi_A(2) - \phi_B(1)\bullet\phi_B(2)]$

$P_{AB}\ \Psi_{nucl\ spin}(A,B)$:

$P_{AB}\ \alpha(A)\bullet\alpha(B) = +\ \alpha(A)\bullet\alpha(B)$

$P_{AB}\ \beta(A)\bullet\beta(B) = +\ \beta(A)\bullet\beta(B)$

$P_{AB}\ 1/\sqrt{2}\{\alpha(A)\bullet\beta(B)+ \beta(A)\bullet\alpha(B)\} = +\ 1/\sqrt{2}\{\alpha(A)\bullet\beta(B) + \beta(A)\bullet\alpha(B)\}$

$P_{AB}\ 1/\sqrt{2}\{\alpha(A)\bullet\beta(B) - \beta(A)\bullet\alpha(B)\} = -\ 1/\sqrt{2}\{\alpha(A)\bullet\beta(B) - \beta(A)\bullet\alpha(B)\}$

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

$P_{AB}\Psi_{vib}(R_{AB}) = +\ \Psi_{vib}(R_{AB})$

$P_{AB}\ F(X_{CM})\bullet G(Y_{CM})\bullet D(Z_{CM}) = +\ F(X_{CM})\bullet G(Y_{CM})\bullet D(Z_{CM})$

Ψ_{TOTAL} =
$\Psi_{elec\ space}(1,2)\bullet\Psi_{elec\ spin}(1,2)\bullet\Psi_{vib}(R_{AB})\bullet Y_{rot\ JM}(\theta,\phi)\bullet\Psi_{nucl\ spin}(A,B)\bullet F(X_{CM})\bullet G(Y_{CM})$

$\bullet D(Z_{CM})$
$P_{12}\Psi_{TOTAL} = -\ \Psi_{TOTAL}$ since electrons are fermions
$P_{AB}\Psi_{TOTAL} = -\ \Psi_{TOTAL}$ if nuclei A and B are fermions

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$\Psi_{elec\ space}(1,2)$	$\Psi_{elec\ spin}(1,2)$	$\Psi_{vib\ v}(R_{AB})$	$Y_{rot\ JM}(\theta,\phi)$	$\Psi_{nucl\ spin}(A,B)$	$F(X_{CM})\bullet G(Y_{CM})\bullet D(Z_{CM})$
$\sigma_g(1)\bullet\sigma_g(2)$ ground $X^1\Sigma_g^+$ P_{12} sym, P_{AB} sym	$\{\alpha(1)\bullet\beta(2) - \beta(1)\bullet\alpha(2)\}/\sqrt{2}$ P_{12} antisym	any v P_{AB} sym	J = even P_{AB} sym	$\{\alpha(A)\bullet\beta(B) - \beta(A)\bullet\alpha(B)\ /\sqrt{2}$ P_{AB} antisym	any n_x, n_y, n_z
$\sigma_g(1)\bullet\sigma_g(2)$ ground $X^1\Sigma_g^+$ P_{12} sym, P_{AB} sym	$\{\alpha(1)\bullet\beta(2) - \beta(1)\bullet\alpha(2)\}/\sqrt{2}$ P_{12} antisym	any v P_{AB} sym	J = odd P_{AB} antisym	$\alpha(A)\bullet\alpha(B)$ $\beta(A)\bullet\beta(B)$ P_{AB} sym $\{\alpha(A)\bullet\beta(B) + \beta(A)\bullet\alpha(B)\ /\sqrt{2}$	any n_x, n_y, n_z
$\{\sigma_g(1)\bullet\sigma_u(2) - \sigma_u(1)\bullet\sigma_g(2)\}/\sqrt{2}$ $b^3\Sigma_u^+$ P_{12} antisym, P_{AB} antisym	$\alpha(1)\bullet\alpha(2)$ $\beta(1)\bullet\beta(2)$ P_{12} sym $\{\alpha(1)\bullet\beta(2) + \beta(1)\bullet\alpha(2)\}/\sqrt{2}$	any v P_{AB} sym	J = even P_{AB} sym	$\alpha(A)\bullet\alpha(B)$ $\beta(A)\bullet\beta(B)$ P_{AB} sym $\{\alpha(A)\bullet\beta(B) + \beta(A)\bullet\alpha(B)\ /\sqrt{2}$	any n_x, n_y, n_z
$\{\sigma_g(1)\bullet\sigma_u(2) - \sigma_u(1)\bullet\sigma_g(2)\}/\sqrt{2}$ $b^3\Sigma_u^+$ P_{12} antisym, P_{AB} antisym	$\alpha(1)\bullet\alpha(2)$ $\beta(1)\bullet\beta(2)$ P_{12} sym $\{\alpha(1)\bullet\beta(2) + \beta(1)\bullet\alpha(2)\}/\sqrt{2}$	any v P_{AB} sym	J = odd P_{AB} antisym	$\{\alpha(A)\bullet\beta(B) - \beta(A)\bullet\alpha(B)\ /\sqrt{2}$ P_{AB} antisym	any n_x, n_y, n_z
$\{\sigma_g(1)\bullet\sigma_u(2) + \sigma_u(1)\bullet\sigma_g(2)\}/\sqrt{2}$ $B^1\Sigma_u^+$ P_{12} sym, P_{AB} antisym	$\{\alpha(1)\bullet\beta(2) - \beta(1)\bullet\alpha(2)\}/\sqrt{2}$ P_{12} antisym	any v P_{AB} sym	J = even P_{AB} sym	$\alpha(A)\bullet\alpha(B)$ $\beta(A)\bullet\beta(B)$ P_{AB} sym $\{\alpha(A)\bullet\beta(B) + \beta(A)\bullet\alpha(B)\ /\sqrt{2}$	any n_x, n_y, n_z
$\{\sigma_g(1)\bullet\sigma_u(2) + \sigma_u(1)\bullet\sigma_g(2)\}/\sqrt{2}$ $B^1\Sigma_u^+$ P_{12} sym, P_{AB} antisym	$\{\alpha(1)\bullet\beta(2) - \beta(1)\bullet\alpha(2)\}/\sqrt{2}$ P_{12} antisym	any v P_{AB} sym	J = odd P_{AB} antisym	$\{\alpha(A)\bullet\beta(B) - \beta(A)\bullet\alpha(B)\ /\sqrt{2}$ P_{AB} antisym	any n_x, n_y, n_z
$\sigma_u(1)\bullet\sigma_u(2)$ very excited $^1\Sigma_g^+$ P_{12} sym, P_{AB} sym	$\{\alpha(1)\bullet\beta(2) - \beta(1)\bullet\alpha(2)\}/\sqrt{2}$ P_{12} antisym	any v P_{AB} sym	J = even P_{AB} sym	$\{\alpha(A)\bullet\beta(B) - \beta(A)\bullet\alpha(B)\ /\sqrt{2}$ P_{AB} antisym	any n_x, n_y, n_z
$\sigma_u(1)\bullet\sigma_u(2)$ $^1\Sigma_g^+$ very excited state P_{12} sym, P_{AB} sym	$\{\alpha(1)\bullet\beta(2) - \beta(1)\bullet\alpha(2)\}/\sqrt{2}$ P_{12} antisym	any v P_{AB} sym	J = odd P_{AB} antisym	$\alpha(A)\bullet\alpha(B)$ $\beta(A)\bullet\beta(B)$ P_{AB} sym $\{\alpha(A)\bullet\beta(B) + \beta(A)\bullet\alpha(B)\ /\sqrt{2}$	any n_x, n_y, n_z

Pauli principle applied to heavy hydrogen, D_2 molecule:

Symmetry with respect to P_{12} is the same as derived for H_2 molecule since electronic functions are unchanged.

Symmetry with respect to P_{AB} is the same for the rotational wavefunction, since only the mass change affects this.

Nuclear spin functions are different because spin of deuteron is 1, hence it is a boson and the number of spin functions is different since m_I = -1, 0, +1 are possible for I=1.

Furthermore, $P_{AB}\Psi_{TOTAL} = - \Psi_{TOTAL}$ if nuclei A and B are bosons (integer spin)

Now consider the nuclear spin of nuclei A and B, the two deuterons. The deuteron has spin I=1 . We can form the eigenfunctions of square of nuclear spin angular momentum $\boldsymbol{I}^2$ from the spin functions that are already eigenfunctions of $\boldsymbol{I}_z$.

Eigenfunctions of $\boldsymbol{I}_z$	M_I		I_{TOT}	Eigenfunctions of $\boldsymbol{I}^2$	P_{AB}
$\alpha(A)\bullet\alpha(B)$	+1 + 1 = 2		2	$\alpha(A)\bullet\alpha(B)$	+
$\beta(A)\bullet\beta(B)$	-1 - 1 = -2		2	$\beta(A)\bullet\beta(B)$	+
$\alpha(A)\bullet\beta(B)$	+1 - 1 = 0	degenerate	2	$1/\sqrt{2}\{\alpha(A)\bullet\beta(B)+ \beta(A)\bullet\alpha(B)\}$	+
$\beta(A)\bullet\alpha(B)$	-1 + 1 = 0	degenerate	1	$1/\sqrt{2}\{\alpha(A)\bullet\beta(B)- \beta(A)\bullet\alpha(B)\}$	-
$\gamma(A)\bullet\gamma(B)$	0 + 0 = 0		0	$\gamma(A)\bullet\gamma(B)$	+
$\alpha(A)\bullet\gamma(B)$	+1+ 0 = 1	degenerate	2	$1/\sqrt{2}\{\alpha(A)\bullet \gamma(B)+ \gamma(A)\bullet\alpha(B)\}$	+
$\gamma(A)\bullet\alpha(B)$	0 + 1 = 1	degenerate	1	$1/\sqrt{2}\{\alpha(A)\bullet \gamma(B)- \gamma(A)\bullet\alpha(B)\}$	-
$\beta(A)\bullet\gamma(B)$	-1+ 0 = -1	degenerate	2	$1/\sqrt{2}\{\gamma (A)\bullet\beta(B)+ \beta(A)\bullet \gamma(B)\}$	+
$\gamma(A)\bullet \beta(B)$	0 - 1 = -1	degenerate	1	$1/\sqrt{2}\{\gamma (A)\bullet\beta(B)- \beta(A)\bullet \gamma(B)\}$	-

Classified the above 9 functions that are eigenfunctions of $\boldsymbol{I}_{TOT}^2$ according to 'symmetric' or 'antisymmetric' with respect to interchange of deuterons A and B, shown respectively as (+) *or* (-)*.*

$P_{AB}\,\Psi_{nucl\ spin}(A,B)$:

$P_{AB}\ \alpha(A)\bullet\alpha(B) = + \alpha(A)\bullet\alpha(B)$

$P_{AB}\ \beta(A)\bullet\beta(B) = + \beta(A)\bullet\beta(B)$

$P_{AB}\ \gamma(A)\bullet\gamma(B) = + \gamma(A)\bullet\gamma(B)$

$P_{AB}\ 1/\sqrt{2}\{\alpha(A)\bullet\beta(B)+ \beta(A)\bullet\alpha(B)\} = + 1/\sqrt{2}\{\alpha(A)\bullet\beta(B) + \beta(A)\bullet\alpha(B)\}$

$P_{AB}\ 1/\sqrt{2}\{\alpha(A)\bullet \gamma(B)+ \gamma(A)\bullet\alpha(B)\} = +1/\sqrt{2}\{\alpha(A)\bullet \gamma(B)+ \gamma(A)\bullet\alpha(B)\}$

$P_{AB}\ 1/\sqrt{2}\{\gamma (A)\bullet\beta(B)+ \beta(A)\bullet \gamma(B)\} = + 1/\sqrt{2}\{\gamma (A)\bullet\beta(B)+ \beta(A)\bullet \gamma(B)\}$

$P_{AB}\ 1/\sqrt{2}\{\alpha(A)\bullet\beta(B) - \beta(A)\bullet\alpha(B)\} = - 1/\sqrt{2}\{\alpha(A)\bullet\beta(B) - \beta(A)\bullet\alpha(B)\}$

$P_{AB}\ 1/\sqrt{2}\{\alpha(A)\bullet \gamma(B)- \gamma(A)\bullet\alpha(B)\} = - 1/\sqrt{2}\{\alpha(A)\bullet \gamma(B)- \gamma(A)\bullet\alpha(B)\}$

$P_{AB}\ 1/\sqrt{2}\{\gamma (A)\bullet\beta(B)- \beta(A)\bullet \gamma(B)\} = - 1/\sqrt{2}\{\gamma (A)\bullet\beta(B)- \beta(A)\bullet \gamma(B)\}$

$P_{12}\Psi_{TOTAL} = - \Psi_{TOTAL}$ since electrons are fermions

$P_{AB}\Psi_{TOTAL} = + \Psi_{TOTAL}$ if nuclei A and B are bosons

$P_{12}\Psi_{TOTAL} = -\Psi_{TOTAL}$ since electrons are fermions

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$\Psi_{elec\ space}(1,2)$	$\Psi_{elec\ spin}(1,2)$	$\Psi_{vib\ v}(R_{AB})$	$Y_{rot\ JM}(\theta,\phi)$	$\Psi_{nucl\ spin}(A,B)$	F•G•D $\mathbf{R}_{CM}$
$\sigma_g(1)\bullet\sigma_g(2)$ ground $X^1\Sigma_g^+$ P_{12} sym, P_{AB} sym	$\{\alpha(1)\bullet\beta(2) - \beta(1)\bullet\alpha(2)\}/\sqrt{2}$ P_{12} antisym	any v P_{AB} sym	J = even P_{AB} sym	$\alpha(A)\bullet\alpha(B)$ $\beta(A)\bullet\beta(B)$ $\gamma(A)\bullet\gamma(B)$ P_{AB} sym $\{\alpha(A)\bullet\beta(B)+\beta(A)\bullet\alpha(B)\}/\sqrt{2}$ $\{\alpha(A)\bullet\gamma(B)+\gamma(A)\bullet\alpha(B)\}/\sqrt{2}$ $\{\gamma(A)\bullet\beta(B)+\beta(A)\bullet\gamma(B)\}/\sqrt{2}$	any n_x, n_y, n_z
$\sigma_g(1)\bullet\sigma_g(2)$ ground $X^1\Sigma_g^+$ P_{12} sym, P_{AB} sym	$\{\alpha(1)\bullet\beta(2) - \beta(1)\bullet\alpha(2)\}/\sqrt{2}$ P_{12} antisym	any v P_{AB} sym	J = odd P_{AB} antisym	$\{\alpha(A)\bullet\beta(B)-\beta(A)\bullet\alpha(B)\}/\sqrt{2}$ $\{\alpha(A)\bullet\gamma(B)-\gamma(A)\bullet\alpha(B)\}/\sqrt{2}$ $\{\gamma(A)\bullet\beta(B)-\beta(A)\bullet\gamma(B)\}/\sqrt{2}$ P_{AB} antisym	any n_x, n_y, n_z
$\{\sigma_g(1)\bullet\sigma_u(2) - \sigma_u(1)\bullet\sigma_g(2)\}/\sqrt{2}$ $b^3\Sigma_u^+$ P_{12} antisym, P_{AB} antisym	$\alpha(1)\bullet\alpha(2)$ $\beta(1)\bullet\beta(2)$ $\{\alpha(1)\bullet\beta(2)+\beta(1)\bullet\alpha(2)\}/\sqrt{2}$ P_{12} sym	any v P_{AB} sym	J = even P_{AB} sym	$\{\alpha(A)\bullet\beta(B)-\beta(A)\bullet\alpha(B)\}/\sqrt{2}$ $\{\alpha(A)\bullet\gamma(B)-\gamma(A)\bullet\alpha(B)\}/\sqrt{2}$ $\{\gamma(A)\bullet\beta(B)-\beta(A)\bullet\gamma(B)\}/\sqrt{2}$ P_{AB} antisym	any n_x, n_y, n_z
$\{\sigma_g(1)\bullet\sigma_u(2) - \sigma_u(1)\bullet\sigma_g(2)\}/\sqrt{2}$ $b^3\Sigma_u^+$ P_{12} antisym, P_{AB} antisym	$\alpha(1)\bullet\alpha(2)$ $\beta(1)\bullet\beta(2)$ $\{\alpha(1)\bullet\beta(2)+\beta(1)\bullet\alpha(2)\}/\sqrt{2}$ P_{12} sym	any v P_{AB} sym	J = odd P_{AB} antisym	$\alpha(A)\bullet\alpha(B)$ $\beta(A)\bullet\beta(B)$ $\gamma(A)\bullet\gamma(B)$ P_{AB} sym $\{\alpha(A)\bullet\beta(B)+\beta(A)\bullet\alpha(B)\}/\sqrt{2}$ $\{\alpha(A)\bullet\gamma(B)+\gamma(A)\bullet\alpha(B)\}/\sqrt{2}$ $\{\gamma(A)\bullet\beta(B)+\beta(A)\bullet\gamma(B)\}/\sqrt{2}$	any n_x, n_y, n_z
$\{\sigma_g(1)\bullet\sigma_u(2) + \sigma_u(1)\bullet\sigma_g(2)\}/\sqrt{2}$ $B^1\Sigma_u^+$ P_{12} sym, P_{AB} antisym	$\{\alpha(1)\bullet\beta(2) - \beta(1)\bullet\alpha(2)\}/\sqrt{2}$ P_{12} antisym	any v P_{AB} sym	J = even P_{AB} sym	$\{\alpha(A)\bullet\beta(B)-\beta(A)\bullet\alpha(B)\}/\sqrt{2}$ $\{\alpha(A)\bullet\gamma(B)-\gamma(A)\bullet\alpha(B)\}/\sqrt{2}$ $\{\gamma(A)\bullet\beta(B)-\beta(A)\bullet\gamma(B)\}/\sqrt{2}$ P_{AB} antisym	any n_x, n_y, n_z
$\{\sigma_g(1)\bullet\sigma_u(2) + \sigma_u(1)\bullet\sigma_g(2)\}/\sqrt{2}$ $B^1\Sigma_u^+$ P_{12} sym, P_{AB} antisym	$\{\alpha(1)\bullet\beta(2) - \beta(1)\bullet\alpha(2)\}/\sqrt{2}$ P_{12} antisym	any v P_{AB} sym	J = odd P_{AB} antisym	$\alpha(A)\bullet\alpha(B)$ $\beta(A)\bullet\beta(B)$ $\gamma(A)\bullet\gamma(B)$ P_{AB} sym $\{\alpha(A)\bullet\beta(B)+\beta(A)\bullet\alpha(B)\}/\sqrt{2}$ $\{\alpha(A)\bullet\gamma(B)+\gamma(A)\bullet\alpha(B)\}/\sqrt{2}$ $\{\gamma(A)\bullet\beta(B)+\beta(A)\bullet\gamma(B)\}/\sqrt{2}$	any n_x, n_y, n_z
$\sigma_u(1)\bullet\sigma_u(2)$ very excited $^1\Sigma_g^+$ P_{12} sym, P_{AB} sym	$\{\alpha(1)\bullet\beta(2) - \beta(1)\bullet\alpha(2)\}/\sqrt{2}$ P_{12} antisym	any v P_{AB} sym	J = even P_{AB} sym	$\alpha(A)\bullet\alpha(B)$ $\beta(A)\bullet\beta(B)$ $\gamma(A)\bullet\gamma(B)$ P_{AB} sym $\{\alpha(A)\bullet\beta(B)+\beta(A)\bullet\alpha(B)\}/\sqrt{2}$ $\{\alpha(A)\bullet\gamma(B)+\gamma(A)\bullet\alpha(B)\}/\sqrt{2}$ $\{\gamma(A)\bullet\beta(B)+\beta(A)\bullet\gamma(B)\}/\sqrt{2}$	any n_x, n_y, n_z
$\sigma_u(1)\bullet\sigma_u(2)$ $^1\Sigma_g^+$ very excited state P_{12} sym, P_{AB} sym	$\{\alpha(1)\bullet\beta(2) - \beta(1)\bullet\alpha(2)\}/\sqrt{2}$ P_{12} antisym	any v P_{AB} sym	J = odd P_{AB} antisym	$\{\alpha(A)\bullet\beta(B)-\beta(A)\bullet\alpha(B)\}/\sqrt{2}$ $\{\alpha(A)\bullet\gamma(B)-\gamma(A)\bullet\alpha(B)\}/\sqrt{2}$ $\{\gamma(A)\bullet\beta(B)-\beta(A)\bullet\gamma(B)\}/\sqrt{2}$ P_{AB} antisym	any n_x, n_y, n_z

2. with the plane of the paper as the xz plane and z axis along line of centers:

			approximate MO (using the sign convention of z axes pointing towards each other)
(a)	CO	$\pi\,2p_y$	$[2p_y(C)+2p_y(O)]$
(b)	F_2	$\pi^*_g\,2p_x$	$[2p_x(F_1)-2p_x(F_2)]$
(c)	F_2	$\pi_u\,2p_x$	$[2p_x(F_1)+2p_x(F_2)]$
(d)	CO	σ^*2p_z	$[2p_z(C)-2p_z(O)]$
(e)	CO	$\pi^*\,2p_y$	$[2p_y(C)-2p_y(O)]$
(f)	O_2	$\pi_u\,2p_y$	$[2p_y(O)+2p_y(O)]$
(g)	HF	σ	$[1s(H)+2s(F)$
(h)	CO	$\pi\,2p_x$	$[2p_x(C)+2p_x(O)]$
(i)	NO	$\sigma 2p_z$	$[2p_z(N)+2p_z(O)]$
(j)	N_2	$\sigma^*_u 2s$	$[2s(N_1) - 2s(N_2)]$
(k)	CO	$\sigma 2s$	$2s(O)$
(l)	F_2	$\sigma_g 2s$	$[2s(F_1) + 2s(F_2)]$
(m)	F_2	$\sigma_g 2p_z$	$[2p_z(F_1)+2p_z(F_2)]$
(n)	CO	$\pi^*\,2p_x$	$[2p_x(C)-2p_x(O)]$
(o)	N_2	$\sigma^*_u 2p_z$	$[2p_z(N_1)-2p_z(N_2)]$
(p)	CO	σ	$[2s(C)+2p_z(O)]$
(q)	F_2	$\sigma^*_u 2p_z$	$[2p_z(F_1)-2p_z(F_2)]$
(r)	HF	σ	$[1s(H)+2p_z(F)]$

3. 19 electrons on K: $1s^2 2s^2\ 2p^6 3s^2 3p^6 4s$

The inner shells remain nearly atomic and we consider them as core, largely undisturbed by bonding. So we have two approximately one-electron H-atom like atoms:

$4s(K_1) + 4s(K_2)$ would give a molecular orbital $\sigma_g 4s$

Consider the angular momenta of the electrons: s=1/2 and s=1/2 can give rise to S=0 or S=1 four combinations altogether, just as for H_2 molecule in part 1 of this problem set. Following the steps in part 1:

The two electrons will have the <u>electronic configuration</u> $(\sigma_g 4s)^2$ leading to the ground <u>electronic state</u> $X^1\Sigma_g^+$ just as shpwn in the figure from the paper from *J. Mol. Spectros.*

$\sigma_g(1)\bullet\sigma_g(2)$ ground $X^1\Sigma_g^+$ P_{12} sym, P_{AB} sym	$\{\alpha(1)\bullet\beta(2) - \beta(1)\bullet\alpha(2)\}/\sqrt{2}$ P_{12} antisym	vibrational states any v P_{AB} sym	rotational states J = odd P_{AB} antisym	nuclear spin states $\{\alpha(A)\bullet\beta(B) - \beta(A)\bullet\alpha(B)\}/\sqrt{2}$ $\{\alpha(A)\bullet\gamma(B)- \gamma(A)\bullet\alpha(B)\}/\sqrt{2}$ $\{\gamma(A)\bullet\beta(B)- \beta(A)\bullet\gamma(B)\}/\sqrt{2}$ P_{AB} antisym

Just as found for H_2 in part 1, we will find, just using just the MO $\sigma_g 4s$ for each K, the other electronic excited states $^3\Sigma_u^+$, $^1\Sigma_u^+$, $^1\Sigma_g^+$ just as given in the table in part 1, except that, rather than a 1s orbital, we have a 4s orbital on the K atom. We do indeed find the $A^1\Sigma_u^+$ and $^1\Sigma_g^+$ in the J. Mol. Spectrosc. figure. The $^3\Sigma_u^+$ state is not shown, although that also must exist.

Where do the other states $b^3\Pi_g$, $B^1\Pi_u$, $^1\Pi_g$, $^1\Delta_g$ come from? Unlike H atom which has no orbitals p or d in the valence shell, K does have relatively low-lying 4p and 3d atomic orbitals it can use to form molecular orbitals. By following the same procedure as in part 1, but using a 4s orbital on the first K atom and a 4p orbital on the second K atom, we will find the combinations that give rise to $b^3\Pi_g$, $B^1\Pi_u$, $^1\Pi_g$, and $^1\Delta_g$. Look at l_1=0 for the 4s and l_2=1 for the 4p on the second K atom are associated with m_1 =0 and m_2 =0, ±1. Right away we can see that for the MO, $\lambda = 0, \pm 1$ can arise from these combinations of m_1 and m_2. And from $\lambda = 0, \pm 1$, the sums of λ could be 0 or 1 or 2. which are Σ, Π, and Δ states respectively. It now only requires doing the combinations, just as we did in part 1 for 1s and 1s, we need to do for 4s and 4p to find out when you can have g or u, S=0 (singlet) or 1 (triplet) combinations by using the fact that electrons are fermions.