1. INTRODUCTION TO QUANTUM MECHANICS
2. ANGULAR MOMENTUM
3. THE HYDROGEN ATOM
4. MATRIX REPRESENTATION OF QUANTUM MECHANICS
5. ELECTRONIC STRUCTURE OF ATOMS
6. APPROXIMATION METHODS
7. **DIATOMIC MOLECULES**
   - **7.1 Born Oppenheimer approximation**
   - 7.2 Electronic Motion in the H_2^+ Molecule Ion: Molecular Orbitals
   - 7.2 Characteristics of Molecular Orbitals: Angular Momentum, Symmetry
   - 7.3 The Electronic Structure of Diatomic Molecules. Molecular Orbital Theory
   - 7.4 Electronic States of Diatomic Molecules
   - 7.5 Nuclear Motion in Diatomic Molecules
     - 7.5.1 The Angular Part: Rotational Motion
     - 7.5.2 The Radial Part: Vibrational Motion
   - 7.6 Molecular States of Diatomic Molecules, Symmetry Including Spin

DIATOMIC MOLECULES

$$\mathcal{H}_{TOTAL} = \mathcal{H}_{\substack{electronic \\ motion}}(r_i, R_j) + \mathcal{H}_{\substack{nuclear \\ motion}}(R_j)$$

$$= \frac{-\hbar^2}{2M_A}\left(\frac{\partial^2}{\partial X_A^2} + \frac{\partial^2}{\partial Y_A^2} + \frac{\partial^2}{\partial Z_A^2}\right) \frac{-\hbar^2}{2M_B}\left(\frac{\partial^2}{\partial X_B^2} + \frac{\partial^2}{\partial Y_B^2} + \frac{\partial^2}{\partial Z_B^2}\right)$$

$$\frac{-\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2}\right) + \cdots$$

$$+\frac{(+Z_A e)(-e)}{r_{1A}} + \frac{(+Z_A e)(-e)}{r_{2A}} + \cdots + \frac{(+Z_B e)(-e)}{r_{1B}} + \frac{(+Z_B e)(-e)}{r_{2B}} + \cdots$$

$$+\frac{(-e)(-e)}{r_{12}} + \frac{(-e)(-e)}{r_{13}} + \cdots + \frac{(+Z_A e)(+Z_B e)}{R_{AB}}$$

$$\mathcal{H}_{TOTAL}\,\Psi(\vec{r}_1, \vec{r}_2, \cdots \vec{R}_A, \vec{R}_B) = E_{TOTAL}\,\Psi(\vec{r}_1, \vec{r}_2, \cdots \vec{R}_A, \vec{R}_B)$$

DIFFERENT FROM ATOM in that there is the motion of nuclei relative to each other and the motion of electrons in the field of nuclei moving relative to each other.

Can SEPARATE OUT CENTER-OF-MASS motion from all relative motion (internal motion, internal degrees of freedom) → TRANSLATION of center of mass with respect to the LABORATORY
→ internal motion

This is the problem

Born-Oppenheimer separation:

Based on disparate masses of electrons and nuclei

$m_p = 1.67265 \times 10^{-24}$ g
$m_e = 9.10953 \times 10^{-28}$ g $>$ factor of 1836!

worse for heavier nuclei

Kinetic energies are very different!

An electron undergoes a very large number of cycles of its motion in the time that it takes a nucleus to undergo a fraction of its cycle of motion.

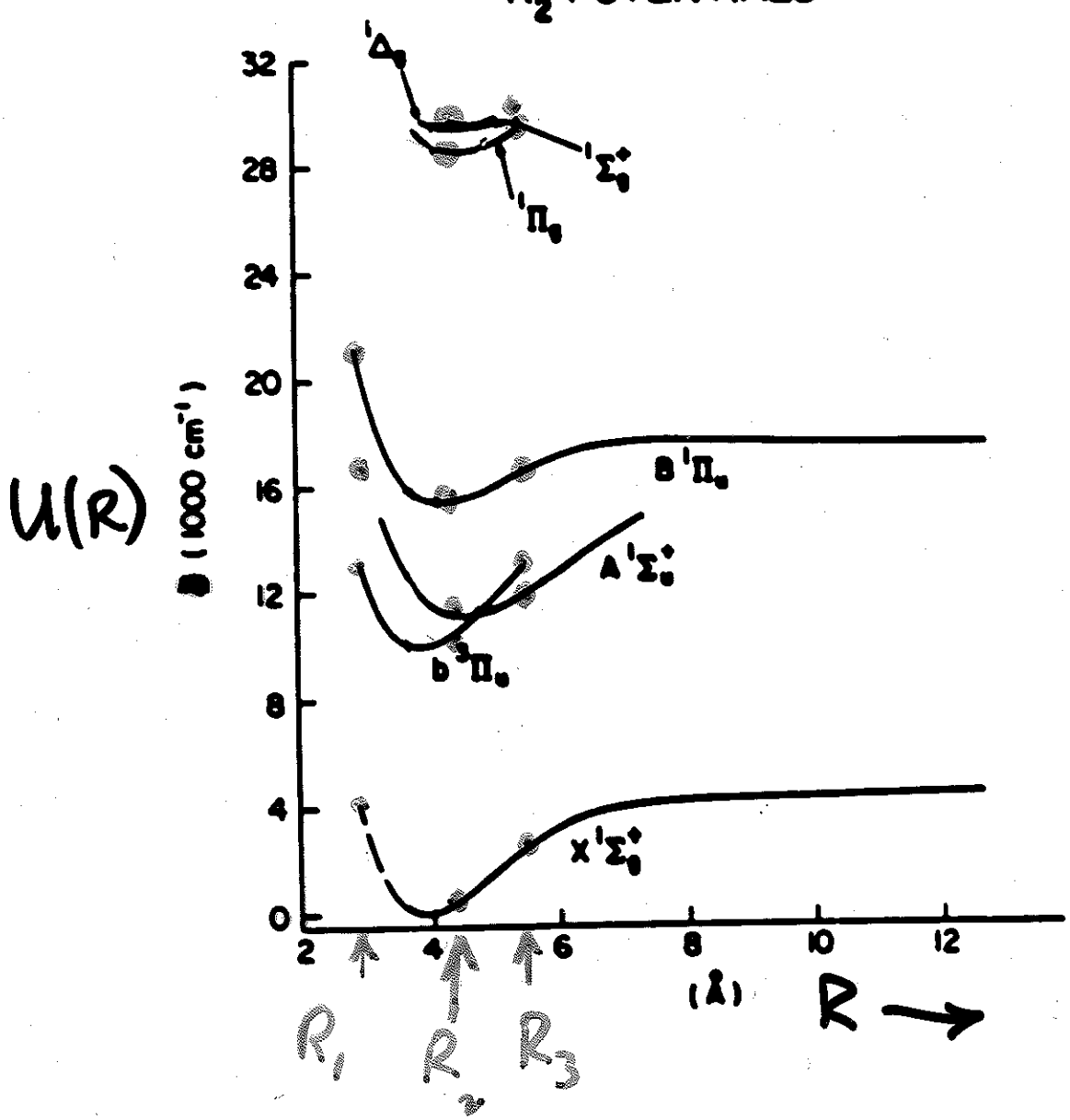
Electrons' point of view: Nuclei are hardly moving

Nuclear point of view: Electrons are moving so fast, they appear as an average charge distribution rather than as individual moving charged particles.

Separation of electronic motion from nuclear motion:

A) Solve electronic motion in presence of fixed rigid nuclear positions:

$$\mathcal{H}_{\text{electronic motion}}(\vec{r}_i, \vec{R}_j = \text{parameters})\,\psi_{elec}(\vec{r}_i, \vec{R}_j = \text{parms}) = U(\vec{R}_j = \text{parms})\,\psi_{elec}(\vec{r}_i, R_j = \text{parms})$$



Sets of Eigenvalues at R_1, R_2, R_3 internuclear distances

B) Solve nuclear motion in the average potential energy provided by the electrons:

$$\left\{ -\frac{\hbar^2}{2M_A}\left(\frac{\partial^2}{\partial X_A^2}+\frac{\partial^2}{\partial Y_A^2}+\frac{\partial^2}{\partial Z_A^2}\right) -\frac{\hbar^2}{2M_B}\left(\frac{\partial^2}{\partial X_B^2}+\frac{\partial^2}{\partial Y_B^2}+\frac{\partial^2}{\partial Z_B^2}\right) + \underbrace{U(R_{AB})}_{\text{solutions to the electronic motion Schrödinger equation.}} \right\} \psi_{\text{nuclear motion}}(\vec{R}_A, \vec{R}_B) = E \psi(\vec{R}_A, \vec{R}_B)$$

TDT

What is left out in using the Born-Oppenheimer separation?

Let us write the Hamiltonian and the functions in simpler notation: use {R} for nuclear coordinates and {r} for electron coordinates:

$\mathcal{H}(R,r)\Psi(R,r) = E\Psi(R,r)$

$$\mathcal{H}(R,r) = \Sigma_\alpha(-(\hbar^2/2M_\alpha)\nabla^2_{R\,\alpha}) + \Sigma_i\,(-(\hbar^2/2m)\nabla^2_{r\,i}) + V(R,r)$$

where V(R,r) includes $V_{eN} + V_{NN} + V_{ee}$

The B-O separation is to consider a simple product $\Psi(R,r) \approx \Psi_e(r;R)\bullet \Psi_N(R)$ <u>which are the solutions of the separate equations for electronic and nuclear motion:</u>

For fixed nuclear positions:

$$\{\Sigma_i\,(-(\hbar^2/2m)\nabla_{ri}^2) + V(R_{parm}, r)\}\Psi_e(r;R_{parm}) = U(R_{parm})\Psi_e(r;R_{parm})\ *$$

The eigenvalues of the electronic motion problem at various values of R are connected together and

the resulting function U(R) serves as the potential energy term for the nuclear motion

$\{\Sigma_\alpha(-(\hbar^2/2M_\alpha)\nabla^2_{R\,\alpha}) + U(R)\}\Psi_N(R) = E\,\Psi_N(R)$ **

If we try the product function in the Schr eqn:

$$\Sigma_\alpha -(\hbar^2/2M_\alpha)\nabla^2_{R\,\alpha}\Psi_e(r;R)\bullet\Psi_N(R) + \Sigma_i -(\hbar^2/2m)\nabla^2_{r\,i}\Psi_e(r;R)\bullet\Psi_N(R) + V(R,r)\,\Psi_e(r;R)\bullet\Psi_N(R) = E\Psi_e(r;R)\bullet\Psi_N(R)$$

then we find,

$$\mathbf{\Sigma_\alpha -(\hbar^2/2M_\alpha)\{\Psi_N(R)\bullet\nabla^2_{R\alpha}\Psi_e(r;R) + 2\nabla_{R\alpha}\Psi_e(r;R)\nabla_{R\alpha}\Psi_N(R) + \Psi_e(r;R)\bullet\nabla^2_{R\alpha}\Psi_N(R)\}} + \Sigma_i -(\hbar^2/2m)\nabla^2_{r\,i}\Psi_e(r;R)\bullet\Psi_N(R) + V(R,r)\,\Psi_e(r;R)\bullet\Psi_N(R) = E\Psi_e(r;R)\bullet\Psi_N(R)$$

The coupling terms

$$\mathbf{\Sigma_\alpha -(\hbar^2/2M_\alpha)\{\Psi_N(R)\bullet\nabla^2_{R\alpha}\Psi_e(r;R) + 2\nabla_{R\alpha}\Psi_e(r;R)\nabla_{R\alpha}\Psi_N(R)}$$

involve derivatives of the electronic wavefunction with respect to the nuclear coordinates.

If we call the sum of the coupling terms taken all together as B, then we can write

$\mathcal{H}(R,r)\ \Psi_e(r;R)\bullet\Psi_N(R) = B$

$+ \Psi_e(r;R)\bullet\Sigma_\alpha(-(\hbar^2/2M_\alpha)\nabla^2_{R\alpha})\ \Psi_N(R)$

$+ \Psi_N(R)\bullet\mathbf{\{\Sigma_i -(\hbar^2/2m)\nabla^2_{ri}+V(R,r)\}\Psi_e(r;R)}$

We recognize the $\mathbf{U(R)\Psi_e(r;R)}$ in eqn *
and put it in:

$\mathcal{H}(R,r)\ \Psi_e(r;R)\bullet\Psi_N(R) = B$

$+ \Psi_e(r;R)\bullet\Sigma_\alpha(-(\hbar^2/2M_\alpha)\nabla^2_{R\alpha})\ \Psi_N(R)$

$+ \Psi_N(R)\bullet\ \mathbf{U(R)\Psi_e(r;R)}$

$\mathcal{H}(R,r)\ \Psi_e(r;R)\bullet\Psi_N(R) = B$

$+ \Psi_e(r;R)\bullet\mathbf{\{\Sigma_\alpha(-(\hbar^2/2M_\alpha)\nabla^2_{R\alpha})+U(R)\}\Psi_N(R)}$

We recognize the $\mathbf{E\Psi_N(R)}$ in eqn **and put it in:

$\mathcal{H}(R,r)\ \Psi_e(r;R)\bullet\Psi_N(R) = B + E\Psi_e(r;R)\bullet\ \Psi_N(R).$

In the adiabatic approximation, one computes the average value of the coupling terms for a given electronic $\Psi_e(r;R)$ and then adds to the nuclear motion Hamiltonian the terms

$\Sigma_\alpha(-(\hbar^2/2M_\alpha)\{\ \langle\mathbf{\Psi_e(r;R)\nabla^2_{R\alpha}\Psi_e(r;R)}\rangle +$

$\langle\mathbf{2\Psi_e(r;R)\nabla_{R\alpha}\Psi_e(r;R)}\rangle\}$

Dissociation energy D_0

in cm^{-1}	H_2	HD	D_2
Born-Oppenheimer	36112.2	36401.5	36745.6
Adiabatic approx	36118.0	36405.7	36748.3
Non-adiab accurate	36114.7	36402.9	36746.2
EXPT	36113.6	36400.5	36744.2

The Born-Oppenheimer approximation is quite acceptable.

(A) Electronic motion in presence of fixed rigid nuclear positions:

$$\left[-\frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial y_1^2}+\frac{\partial^2}{\partial z_1^2}\right) -\frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial x_2^2}+\frac{\partial^2}{\partial y_2^2}+\frac{\partial^2}{\partial z_2^2}\right) + \cdots + \frac{(Z_A e)(-e)}{r_{1A}} + \frac{(+Z_B e)(-e)}{r_{1B}} + \frac{(Z_A e)(-e)}{r_{2A}} + \frac{(Z_B e)(-e)}{r_{2B}} + \frac{(Z_A e)(Z_B e)}{R_{AB}} + \frac{e^2}{r_{12}} + \cdots \right] \Psi(\vec{r}_1, \vec{r}_2, R_{AB}=\text{parameter}) = U(R_{AB})\,\Psi(\vec{r}_1, \vec{r}_2, R_{AB})$$

We saw what the $U(R_{AB})$ looked like. What do the functions look like? Let us do only one-electron, the hydrogen molecule ion with stationary nuclei:

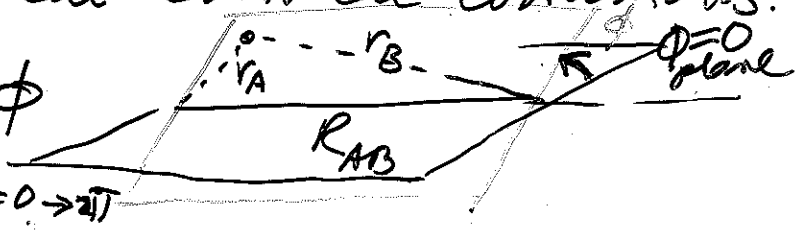
$$\left\{ -\frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right) - \frac{Z_A e^2}{r_A} - \frac{Z_B e^2}{r_B} + \frac{Z_A Z_B e^2}{R_{AB}} \right\} \Psi = U(R_{AB})\,\Psi(\vec{r}_1, R_{AB})$$

This can be solved by separation of variables! if we choose the elliptical confocal coordinates:

$$\rho = \frac{r_A + r_B}{R_{AB}} \qquad \rho = 1 \to \infty$$

$$\xi = \frac{r_A - r_B}{R_{AB}} \qquad \xi = -1 \to +1$$

$$\phi \qquad \phi = 0 \to 2\pi$$



p = constant : ellipsoids of revolution
foci at protons
q = constant : hyperboloids of revolution

Use this transformation of coordinates to get

$$\frac{\partial}{\partial p}\left[(p^2-1)\frac{\partial \Psi}{\partial p}\right] + \frac{\partial}{\partial q}\left[(1-q^2)\frac{\partial \Psi}{\partial q}\right] + \frac{p^2-q^2}{(p^2-1)(1-q^2)}\frac{\partial^2 \Psi}{\partial \phi^2} - \frac{1}{2}\{(p^2-q^2)[U(R)R^2 - R] - 4pR\}\Psi = 0$$

SEPARATION OF VARIABLES:

Assume a solution of the form

$$\Psi(p,q,\phi) = P(p)\cdot Q(q)\cdot \Phi(\phi)$$

in which case we find the Schrödinger equation for the one-electron hydrogen molecule ion separates into three equations to be solved:

$$\frac{d^2\Phi}{d\phi^2} = -\lambda^2 \Phi(\phi)$$ is one of them

Solution to this one is obtained just like always, by insisting that the function $\Phi(\phi)$ must be single-valued

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{i\lambda\phi}$$

where λ necessarily has to have values

$\lambda = 0, \pm 1, \pm 2, \pm 3, \ldots$

The component of the angular momentum of the electron along the internuclear axis in the diatomic molecule H_2^+,

$$\frac{\hbar}{i}\frac{\partial}{\partial\phi}$$

has the same eigenfunctions

$$\frac{\hbar}{i}\frac{\partial}{\partial\phi}\Phi(\phi) = \lambda\hbar\,\Phi(\phi)$$

The equations in ρ and η are exactly soluble: for any parameter R they lead to the functions $P(\rho)$ and $Q(\eta)$ and the eigenvalues $U(R)$

Now let us examine the states and their characteristics

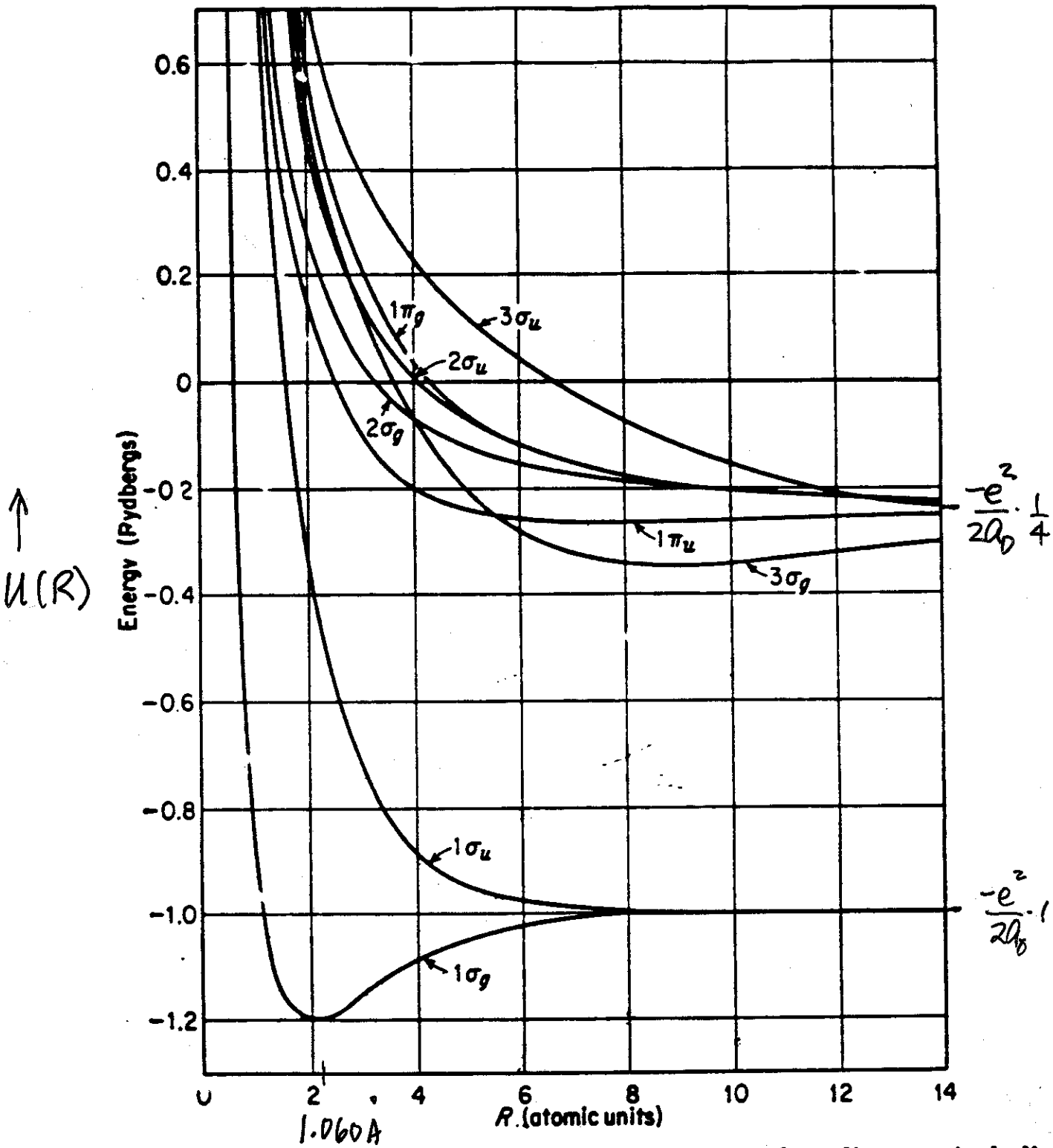


FIG. 1-5. Lowest energy levels of H_2^+ as function of internuclear distance, includin internuclear repulsive energy.

$$\frac{e^2}{2a_0} = 1 \text{ Rydberg}$$

$$\psi(\rho, q, \phi) = \frac{e^{i\lambda\phi}}{\sqrt{2\pi}} \cdot P(\rho) \cdot Q(q)$$

where $\lambda = 0, \pm 1, \pm 2, \ldots\ldots$

i_{op} replace electron coords xyz (relative to fixed nuclear framework) by $-x, -y, -z$

i_{op} $F(\phi) \cdot P(\rho) \cdot Q(q) = (+) F(\phi) \cdot P(\rho) \cdot Q(q)$ call it g

or else $(-) F(\phi) \cdot P(\rho) \cdot Q(q)$ call it u

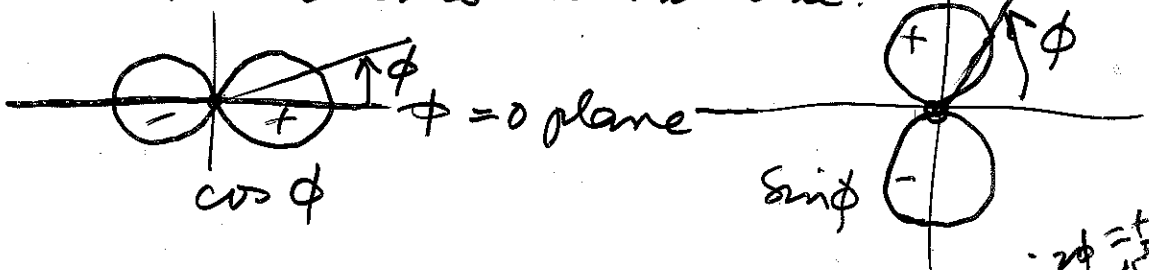
$\lambda = 0$ can be g or u

$\lambda = \pm 1$ can be g or u

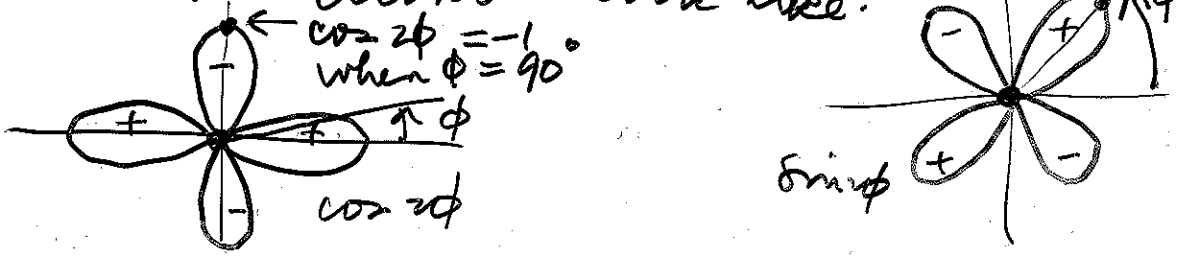
Real functions $\frac{e^{i\lambda\phi} + e^{-i\lambda\phi}}{2} = \cos(\lambda\phi)$

minus $\Rightarrow \sin(\lambda\phi)$

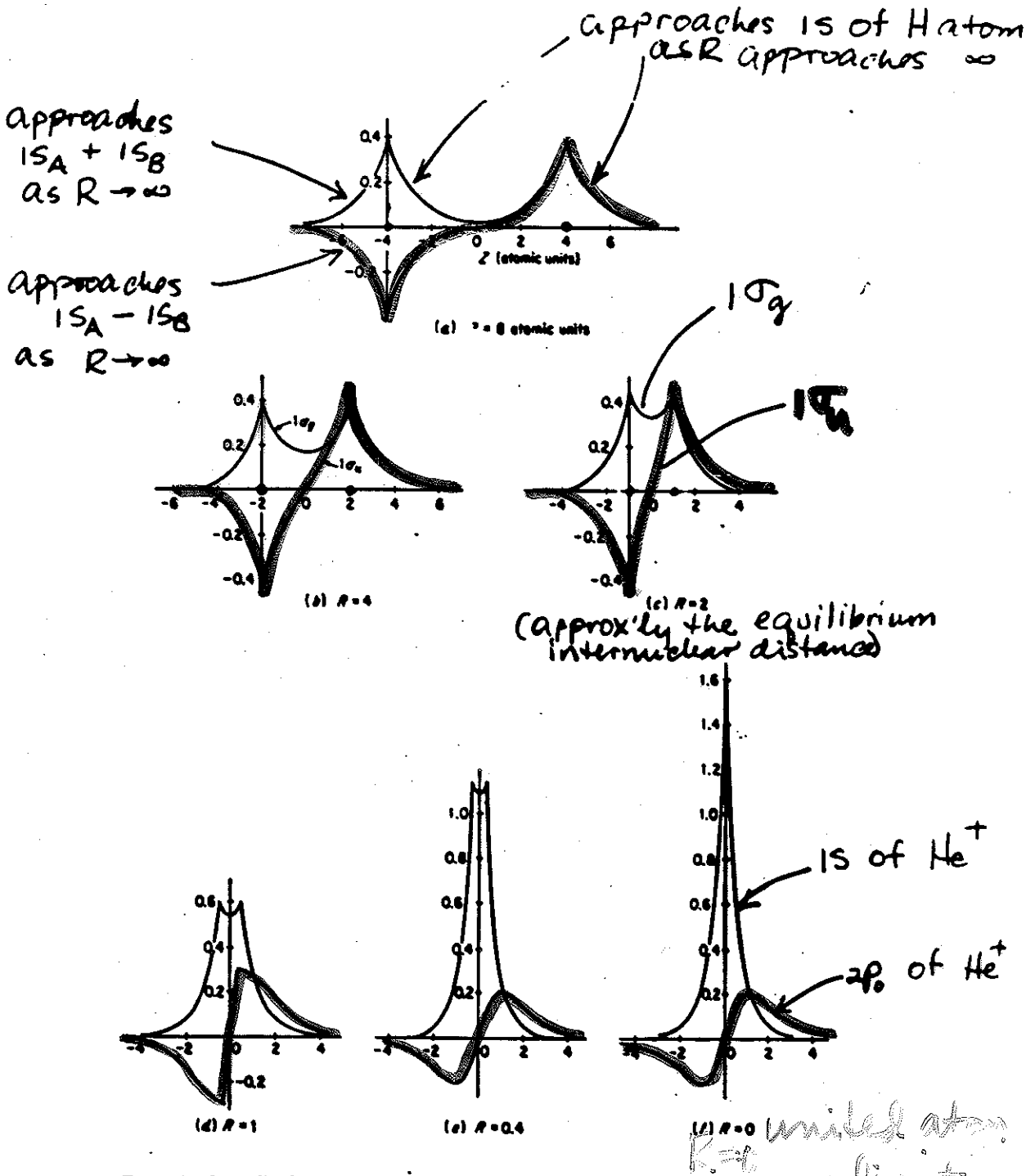
$\lambda = \pm 1$ real functions look like:



$\lambda = \pm 2$ real functions look like:



Normalized functions for H_2^+ for various internuclear distances



(approx'ly the equilibrium internuclear distance)

united atom limit

FIG. 1-3. Normalized wave functions for $1\sigma_g$ and $1\sigma_u$ states of H_2^+, along internuclear axis, for various internuclear separations.

Along the line which is the internuclear axis, a plot of the function $1\sigma_g$ and $1\sigma_u$ (in red), as R_{AB} is changed

In the context of the Born-Oppenheimer approximation we write the complete total wavefunction (space coordinates) of the H_2^+ ion:

$$\underset{\text{TOTAL}}{\Psi}(\vec{r},\vec{R}) = \underbrace{P(\rho)\cdot Q(\rho)\cdot \underset{\lambda}{\Phi}(\phi)}_{\text{electronic motion}} \cdot \underbrace{\underset{n}{S}(R)\, \underset{JM_J}{Y}(\theta,\phi)}_{\text{nuclear relative motion}} \cdot \underbrace{T(X_{cm} Y_{cm} Z_{cm})}_{\text{center of mass translation relative to a fixed LABORATORY axis in the container}}$$

$\frac{\hbar}{i}\frac{\partial}{\partial\phi}$ has eigenvalues $\lambda\hbar$ for electron component of angular momentum about the internuclear axis

neglecting electron spin and nuclear spin, so far

$\frac{\hbar}{i}\frac{\partial}{\partial\phi'}$ has eigenvalues $M_J\hbar$ for nuclear component of rotational angular momentum about a fixed axis through the center of mass. Rotational energy depends on $\frac{J(J+1)\hbar^2}{2\mu R^2}$

$M_J = -J, \cdots +J$

1. INTRODUCTION TO QUANTUM MECHANICS
2. ANGULAR MOMENTUM
3. THE HYDROGEN ATOM
4. MATRIX REPRESENTATION OF QUANTUM MECHANICS
5. ELECTRONIC STRUCTURE OF ATOMS
6. APPROXIMATION METHODS
7. DIATOMIC MOLECULES
    - 7.1 Born Oppenheimer approximation
    - 7.2 Electronic Motion in the H_2^+ Molecule Ion: Molecular Orbitals
    - **7.2 Characteristics of Molecular Orbitals: Angular Momentum, Symmetry**
    - 7.3 The Electronic Structure of Diatomic Molecules. Molecular Orbital Theory
    - 7.4 Electronic States of Diatomic Molecules
    - 7.5 Nuclear Motion in Diatomic Molecules
        - 7.5.1 The Angular Part: Rotational Motion
        - 7.5.2 The Radial Part: Vibrational Motion
    - 7.6 Molecular States of Diatomic Molecules, Symmetry Including Spin

electronic states

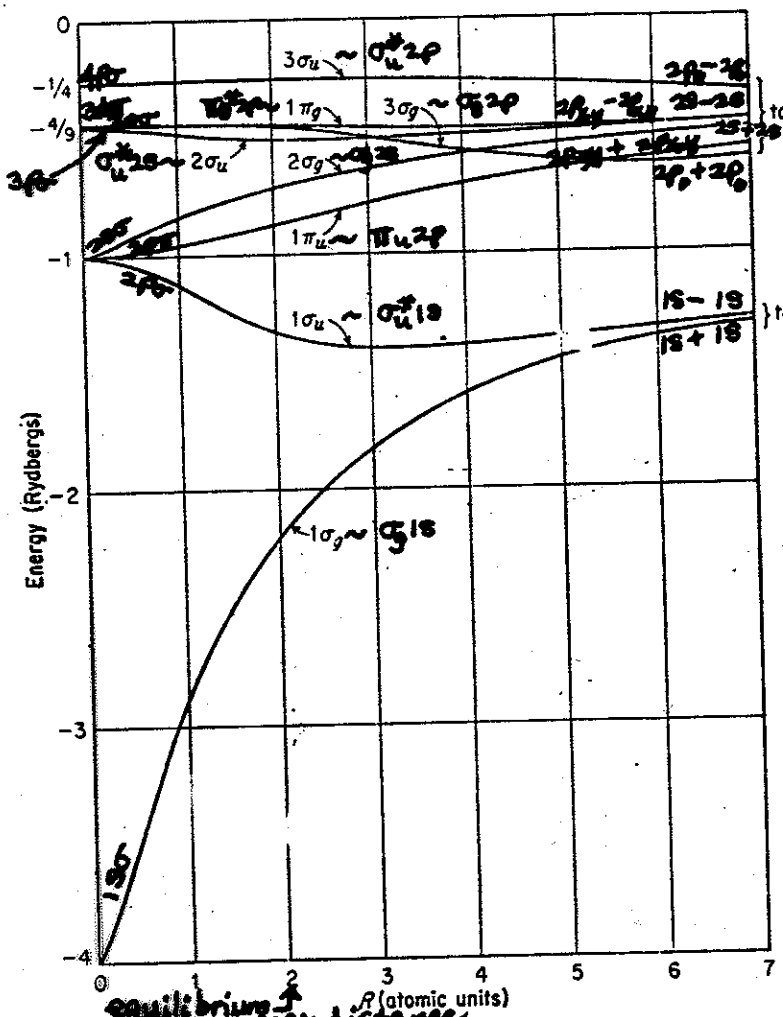
SUMMARY of [one-electron functions and energies] for diatomic molecule H_2^+:

1. Just as in atoms, symbols are associated with values of λ

λ	0	± 1	± 2	± 3	...
symbol	σ	π	δ	ϕ	...
upper case Λ	Σ	Π	Δ	Φ	...

2. Energy dependson λ^2 since all 3 equations contain not λ but λ^2. This means that except for σ states, each state is doubly degenerate
   atoms have L diatomic molecule have L
   atoms have M_L diatomic molecule have λ
3. Symmetry properties
   $i_g \Psi(p,q,\phi) = +\Psi(p,q,\phi)$ gerade (g)
   or else $-\Psi(p,q,\phi)$ ungerade (u)
   $i_g \Psi(1\sigma_g) = +\Psi(1\sigma_g)$
   $i_g \Psi(1\sigma_u) = -\Psi(1\sigma_u)$
4. At $R \to \infty$ the energy levels converge to $\frac{-e^2}{2a_0}$, $-\frac{1}{4}\frac{e^2}{2a_0}$, $-\frac{1}{9}\frac{e^2}{2a_0}$, $\cdots -\frac{Z^2}{n^2}\frac{e^2}{2a_0}$ one of the levels of the hydrogen atom
5. At $R=0$ the levels and the functions become those of the united atom, a He^+ ion

Correlation Diagram for H_2^+



4s, 4p, 4d, 4f
3s, 3p, 3d
2s, 2p
1s
He^+ (UNITED ATOM)

2s, 2p
1s
H + proton (SEPARATED ATOMS) at $R = \infty$

Lowest energy levels of H_2^+ as function of internuclear distance. Internuclear repulsive energy not included.

1. INTRODUCTION TO QUANTUM MECHANICS
2. ANGULAR MOMENTUM
3. THE HYDROGEN ATOM
4. MATRIX REPRESENTATION OF QUANTUM MECHANICS
5. ELECTRONIC STRUCTURE OF ATOMS
6. APPROXIMATION METHODS
7. DIATOMIC MOLECULES
    - 7.1 Born Oppenheimer approximation
    - 7.2 Electronic Motion in the H_2^+ Molecule Ion: Molecular Orbitals
    - 7.2 Characteristics of Molecular Orbitals: Angular Momentum, Symmetry
    - **7.3 The Electronic Structure of Diatomic Molecules. Molecular Orbital Theory**
    - 7.4 Electronic States of Diatomic Molecules
    - 7.5 Nuclear Motion in Diatomic Molecules
        - 7.5.1 The Angular Part: Rotational Motion
        - 7.5.2 The Radial Part: Vibrational Motion
    - 7.6 Molecular States of Diatomic Molecules, Symmetry Including Spin

Molecular Orbital Theory

We have found that for a one-electron homonuclear diatomic molecule such as the H_2^+ molecule ion, the Schrödinger equation for the electronic motion is separable into 3 variables and can be solved exactly.
For the more general diatomic molecule with more than one electron, with the nuclei frozen at fixed positions, the equation to be solved is:

$$\mathcal{H}(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{R}_{AB}) \Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{R}_{AB}) = U(\mathbf{R}_{AB}) \Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{R}_{AB})$$

where $\mathbf{R}_{AB}$ is the distance between stationary nuclei

$$\mathcal{H}(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{R}_{AB}) =$$
$$-(\hbar^2/2m) [\partial^2/\partial x_1^2 + \partial^2/\partial y_1^2 + \partial^2/\partial z_1^2 +]$$
$$-(\hbar^2/2m) [\partial^2/\partial x_2^2 + \partial^2/\partial y_2^2 + \partial^2/\partial z_2^2 +] + ...$$
$$-Z_A e^2/ r_{1A} - Z_B e^2/r_{1B} - Z_A e^2/ r_{2A} - Z_B e^2/r_{2B} + ...$$
$$+ e^2/r_{12} + e^2/r_{13} + ... + Z_A Z_B e^2/\mathbf{R}_{AB}$$

As in the case of many electron atoms, we can use the one-electron-at-a-time self-consistent field approach, that is, we use separation of variables so that instead of one equation in 3N variables, we can solve N equations, each one in the variable coordinates of only one electron. The interelectronic repulsion terms that connect electron 4 (for example) to all the other electrons are treated, as in the many-electron atom, by assuming that electron 4 sees only an average field due to the $\Psi^*\Psi$ of each of the other electrons in the presence of all the nuclei. As we solve the Schrödinger equation for each electron in turn, we find its $\Psi^*\Psi$, which is then used to provide the field in solving the equations for the others, until an internally consistent set of $\Psi^*\Psi$ is found for each of the N electrons. That is why the method is called a SELF-CONSISTENT FIELD method.

This function Ψ for one electron at a time is called a MOLECULAR ORBITAL, the same name as the wavefunctions for the true one-electron H_2^+ system.

And, the functions Ψ will look like the exact solutions for H_2^+ system, with a

$$(1/\sqrt{2\pi})\exp[i\lambda\phi]$$

for the ϕ part, just as in the in the exact solutions for H_2^+ system

This is analogous to atomic orbitals having the same $Y_{\ell m}(\theta,\phi)$ as the exactly soluble hydrogen atom Schrödinger equation when we use the central field approximation.

$\{-(\hbar^2/2m)\,[\partial^2/\partial x_1^2 + \partial^2/\partial y_1^2 + \partial^2/\partial z_1^2] + V(\mathbf{r}_1, \mathbf{R}_{AB},$ integrated $\Psi^*\Psi$ of all other *N-1* electrons)$\}$

$$\Psi(\mathbf{r}_1, \mathbf{R}_{AB}) = \varepsilon_1\,(\mathbf{R}_{AB})\,\Psi(\mathbf{r}_1, \mathbf{R}_{AB})$$

In doing this self-consistent field calculation, we have to start with a functional form for $\Psi(\mathbf{r}_1, \mathbf{R}_{AB})$ for one electron at a time (a MOLECULAR ORBITAL). We choose to write this Ψ as a linear combination of atomic orbitals (LCAO) so as to have a description that is, from the outset, close to the description of the original atoms that formed the molecule.

$\Psi_{MO1} = c_1\,\psi_{AO1} + c_2\,\psi_{AO2} + c_3\,\psi_{AO3} + \ldots$

And we solve the above one-electron equation by ensuring that we have the best values for c_1 c_2 c_3 ... by using the VARIATIONAL METHOD, i.e., finding the minimum value of ε_1 by imposing the condition for an extremum, $\partial\varepsilon_1 / \partial c_1 = 0$, $\partial\varepsilon_1 / \partial c_2 = 0$, $\partial\varepsilon_1 / \partial c_3 = 0$, etc. so that we end up with the best combination of atomic orbitals to describe the MOLECULAR ORBITAL.

The results of such calculations (MOLECULAR ORBITALS) are shown in the following pages.

H_2 WAVEFUNCTIONS OF DIFFERENT CONFIGURATIONS FORMED FROM 1s HYDROGEN ORBITALS

We had previously found that the H_2^+ functions in the simple MO scheme were:

$$\sigma_g = \frac{\phi_A + \phi_B}{\sqrt{2 + 2S}} \quad \text{and} \quad \sigma_u = \frac{\phi_A - \phi_B}{\sqrt{2 - 2S}}$$

In H_2 molecule there are 2 electrons and if we use the H_2^+ one-electron functions (molecular orbitals) there are four spin-orbitals which are possible:

$$\sigma_g\alpha \quad \sigma_g\beta \quad \sigma_u\alpha \text{ and } \sigma_u\beta$$

P_{12}

Putting electrons into these spin-orbitals, we get the following possible (allowed by Pauli principle) configurations:

1) $\sigma_g\alpha$ and $\sigma_g\beta \rightarrow \sigma_g(1)\sigma_g(2) \cdot \dfrac{\alpha(1)\beta(2) - \beta(1)\alpha(2)}{\sqrt{2}}$

sym. space X antisym. spin

2) $\sigma_u\alpha$ and $\sigma_u\beta \rightarrow \sigma_u(1)\sigma_u(2) \cdot \dfrac{\alpha(1)\beta(2) - \beta(1)\alpha(2)}{\sqrt{2}}$

sym. antisym.

3) $\sigma_g\alpha$ and $\sigma_u\alpha \rightarrow \dfrac{\sigma_g(1)\sigma_u(2) - \sigma_u(1)\sigma_g(2)}{\sqrt{2}} \cdot \alpha(1)\alpha(2)$

antisym. sym.

4) $\sigma_g\beta$ and $\sigma_u\beta \rightarrow \dfrac{\sigma_g(1)\sigma_u(2) - \sigma_u(1)\sigma_g(2)}{\sqrt{2}} \cdot \beta(1)\beta(2)$

antisym. sym.

5) $\sigma_g\alpha$ and $\sigma_u\beta$ or $\sigma_u\alpha$ and $\sigma_g\beta$ $\rightarrow \dfrac{\sigma_g(1)\sigma_u(2) - \sigma_u(1)\sigma_g(2)}{\sqrt{2}} \cdot \dfrac{\alpha(1)\beta(2) + \beta(1)\alpha(2)}{\sqrt{2}}$

antisym. sym.

6) $\dfrac{\sigma_g(1)\sigma_u(2) + \sigma_u(1)\sigma_g(2)}{\sqrt{2}} \cdot \dfrac{\alpha(1)\beta(2) - \beta(1)\alpha(2)}{\sqrt{2}}$

sym. antisym.

Expanded out in terms of ϕ_A and ϕ_B, the symmetry or antisymmetry of the space part becomes obvious: with respect to P_{12}

1) $\sigma_g(1)\sigma_g(2) = \dfrac{\phi_A(1)\phi_B(2) + \phi_B(1)\phi_A(2) + \phi_A(1)\phi_A(2) + \phi_B(1)\phi_B(2)}{2(1+S)}$ sym.

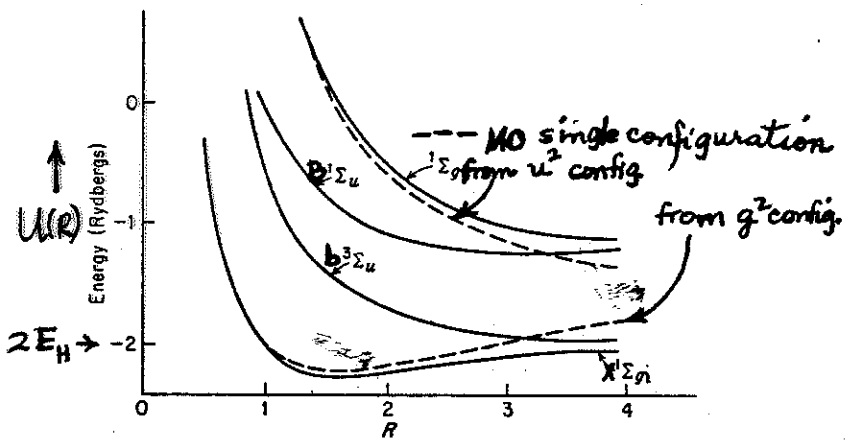
2) $\sigma_u(1)\sigma_u(2) = \dfrac{-\phi_A(1)\phi_B(2) - \phi_B(1)\phi_A(2) + \phi_A(1)\phi_A(2) + \phi_B(1)\phi_B(2)}{2(1+S)}$ sym.

3), 4) and 5)

$$\frac{\sigma_g(1)\sigma_u(2) - \sigma_u(1)\sigma_g(2)}{\sqrt{2}} = \frac{-\phi_A(1)\phi_B(2) + \phi_B(1)\phi_A(2)}{\sqrt{2(1-S^2)}} \quad \text{antisym.}$$

6) $$\frac{\sigma_g(1)\sigma_u(2) + \sigma_u(1)\sigma_g(2)}{\sqrt{2}} = \frac{\phi_A(1)\phi_A(2) - \phi_B(1)\phi_B(2)}{\sqrt{2(1-S^2)}} \quad \text{sym.}$$

Configuration:			term symbol	
1)	g^2 ↑↓	S = 0	$X\ ^1\Sigma_g^+$	ground state
2)	u^2 ↑↓	S = 0	$?\ ^1\Sigma_g^+$	very high energy state
3),4) and 5)				
	gu ↑↑	S = 1	$b\ ^3\Sigma_u^+$	lowest-lying triplet
6)	gu ↑↓	S = 0	$B\ ^1\Sigma_u^+$	



P_{AB}

So far we have considered symmetry or antisymmetry with respect to interchange of two electrons. We can also consider the symmetry of these electronic wavefunctions with respect to interchange of nuclei A and B: By inspection we see that with respect to interchange of nuclei A and B, these electronic states have the following symmetry:

1) symmetric
2) symmetric
3) 4) & 5) antisymmetric
6) antisymmetric

Note that Σ_g^+ states are symmetric with respect to interchange of identical nuclei whereas Σ_u^+ states are antisymmetric:

$$P_{AB}\,\psi_{elec} = (\Sigma^{\pm})(g \text{ or } u)\,\psi_{elec} = \pm\psi_{elec}$$

Symmetry properties of electronic wavefunctions of diatomic molecules

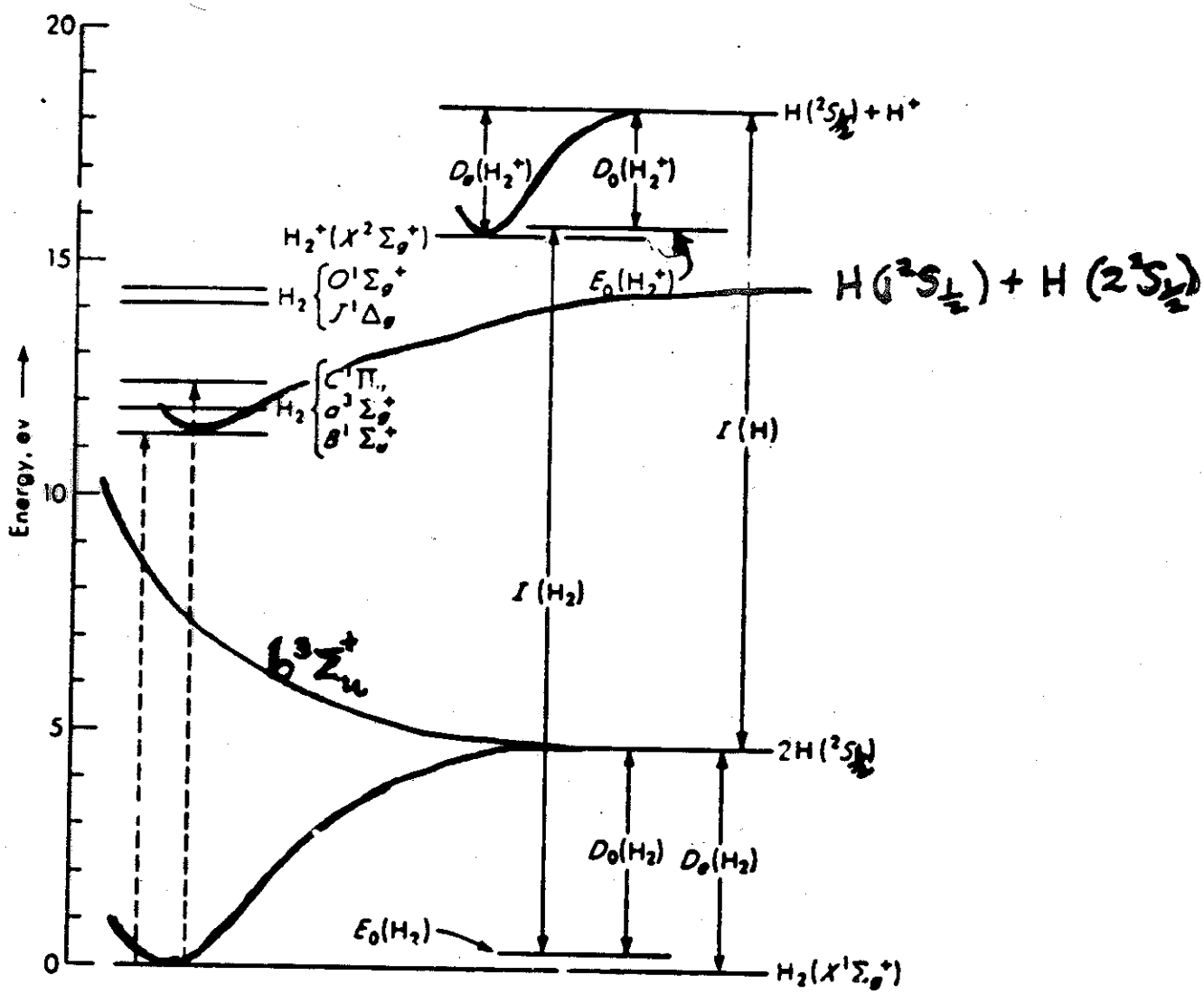
OPERATION		RESULT
I	inversion of all space-fixed coordinates; that is, $(x,y,z) \rightarrow (-x,-y,-z)$ and $(X,Y,Z) \rightarrow (-X,-Y,-Z)$	$I\,\psi_{\text{elec}}^{\text{space}} = (\pm)\,\psi_{\text{elec}}^{\text{space}}$ as in $\Sigma^{(\pm)}$, known as $\pi^{\pm}$, electronic parity ($\pm$ ← sign of Λ)
$\infty\sigma_v$	reflection of molecule-fixed electronic coords.	$\sigma_v\,\psi_{\text{elec}}^{\text{space}} = \pm\,\psi_{\text{elec}}^{\text{space}}$ exactly same result as above
P_{12}	interchange of electrons 1 and 2	$P_{12}\,\psi_{\text{elec}}^{\text{space}}\cdot\psi_{\text{elec}}^{\text{spin}} = (-)\,\psi_{\text{elec}}^{\text{space}}\cdot\psi_{\text{elec}}^{\text{spin}}$ ← electrons are FERMIONS
		$P_{12}\,\psi_{\text{elec}}^{\text{spin}} = (\pm)\,\psi_{\text{elec}}^{\text{spin}}$ as in ORTHO helium or PARA helium

---

and, in addition, when the 2 nuclei are identical we also have the following:

i	inversion of molecule-fixed electronic coords (same as inversion of space-fixed electronic coords; that is, change $(x,y,z) \rightarrow (-x,-y,-z)$)	$i\,\psi_{\text{elec}}^{\text{space}} = (\pm)\,\psi_{\text{elec}}^{\text{space}}$ or (g/u) as in Σ_g, Π_g ...
P_{AB} or ∞C_2	interchange of nuclei A & B which are indistinguishable; rotation about an axis $\perp$ to line of centers	$P_{AB}\,\psi_{\text{elec}}^{\text{space}} = (\pm)\,\psi_{\text{elec}}^{\text{space}} = \left(\Sigma^{\pm}\right)\left(g/u\right)\psi_{\text{elec}}^{\text{space}}$ ← product of these two

Relative energies of H_2 , H_2^+ and H atoms



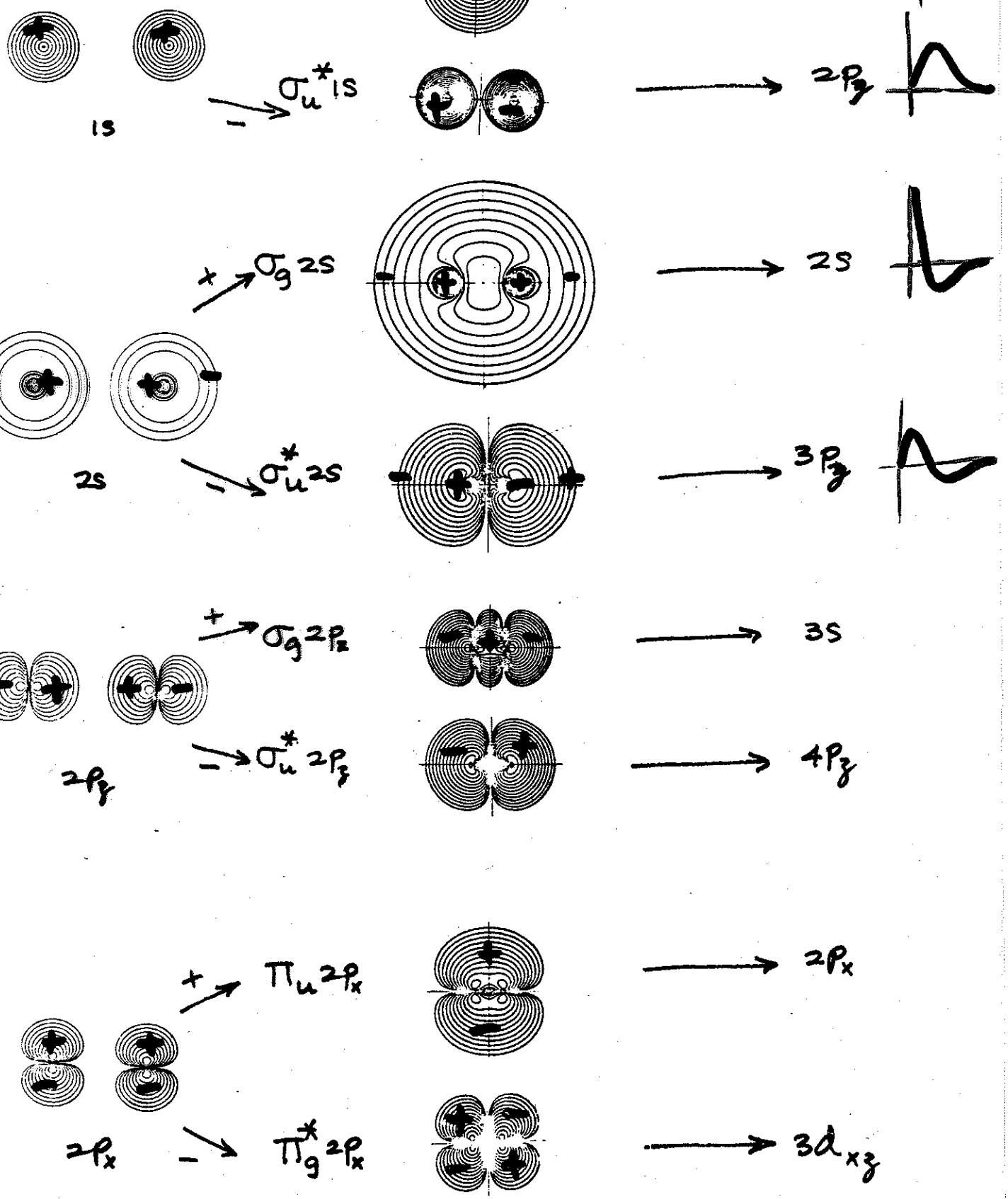
Some stable spectroscopic states of the hydrogen molecule. The dashed arrows show two symmetry- and spin-allowed electronic transitions. The diagram also shows relative energies of H_2^+ and some of its fragments.

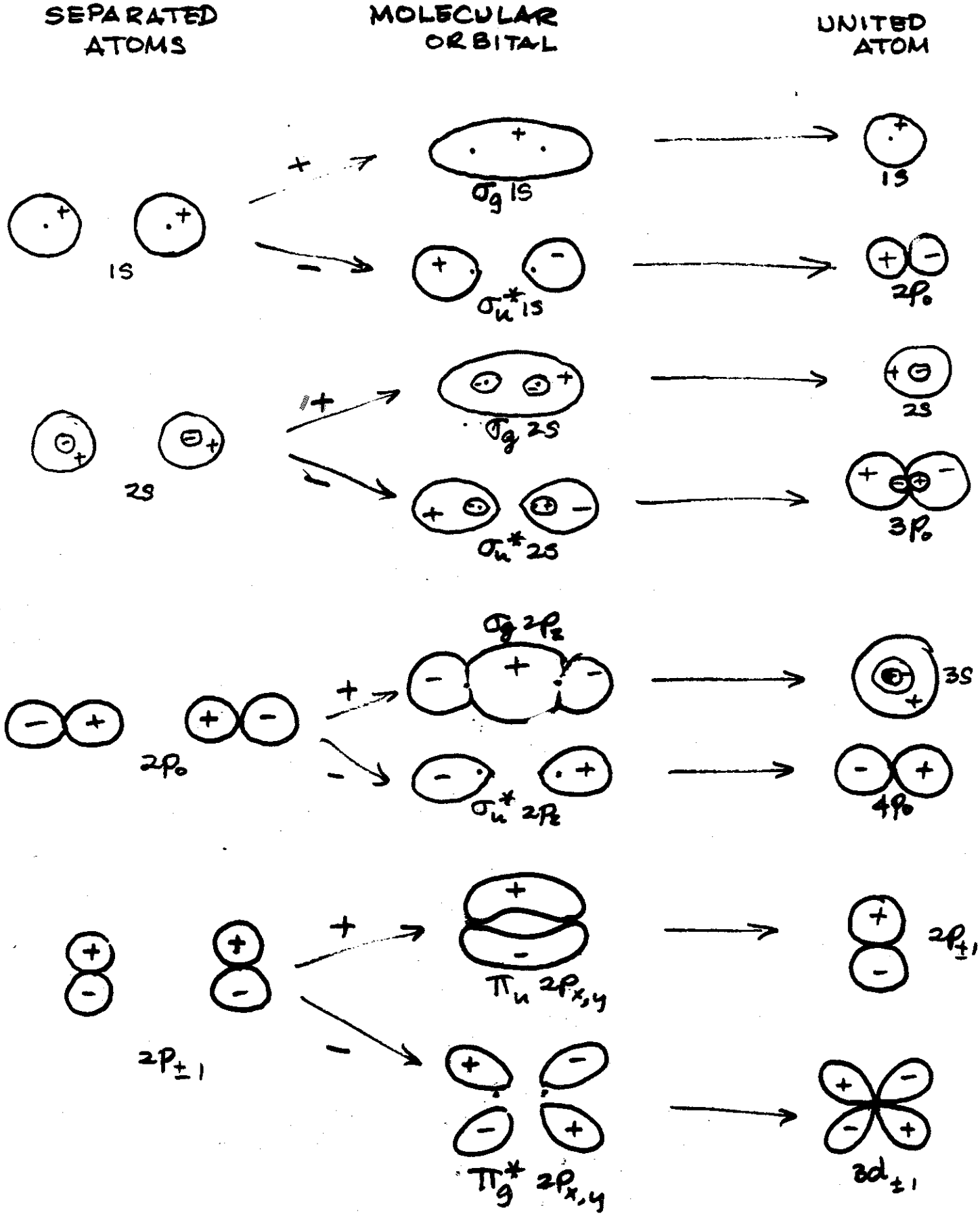
1. INTRODUCTION TO QUANTUM MECHANICS
2. ANGULAR MOMENTUM
3. THE HYDROGEN ATOM
4. MATRIX REPRESENTATION OF QUANTUM MECHANICS
5. ELECTRONIC STRUCTURE OF ATOMS
6. APPROXIMATION METHODS
7. DIATOMIC MOLECULES
    - 7.1 Born Oppenheimer approximation
    - 7.2 Electronic Motion in the H_2^+ Molecule Ion: Molecular Orbitals
    - 7.2 Characteristics of Molecular Orbitals: Angular Momentum, Symmetry
    - 7.3 The Electronic Structure of Diatomic Molecules. Molecular Orbital Theory
    - **7.4 Electronic States of Diatomic Molecules**
    - 7.5 Nuclear Motion in Diatomic Molecules
        - 7.5.1 The Angular Part: Rotational Motion
        - 7.5.2 The Radial Part: Vibrational Motion
    - 7.6 Molecular States of Diatomic Molecules, Symmetry Including Spin

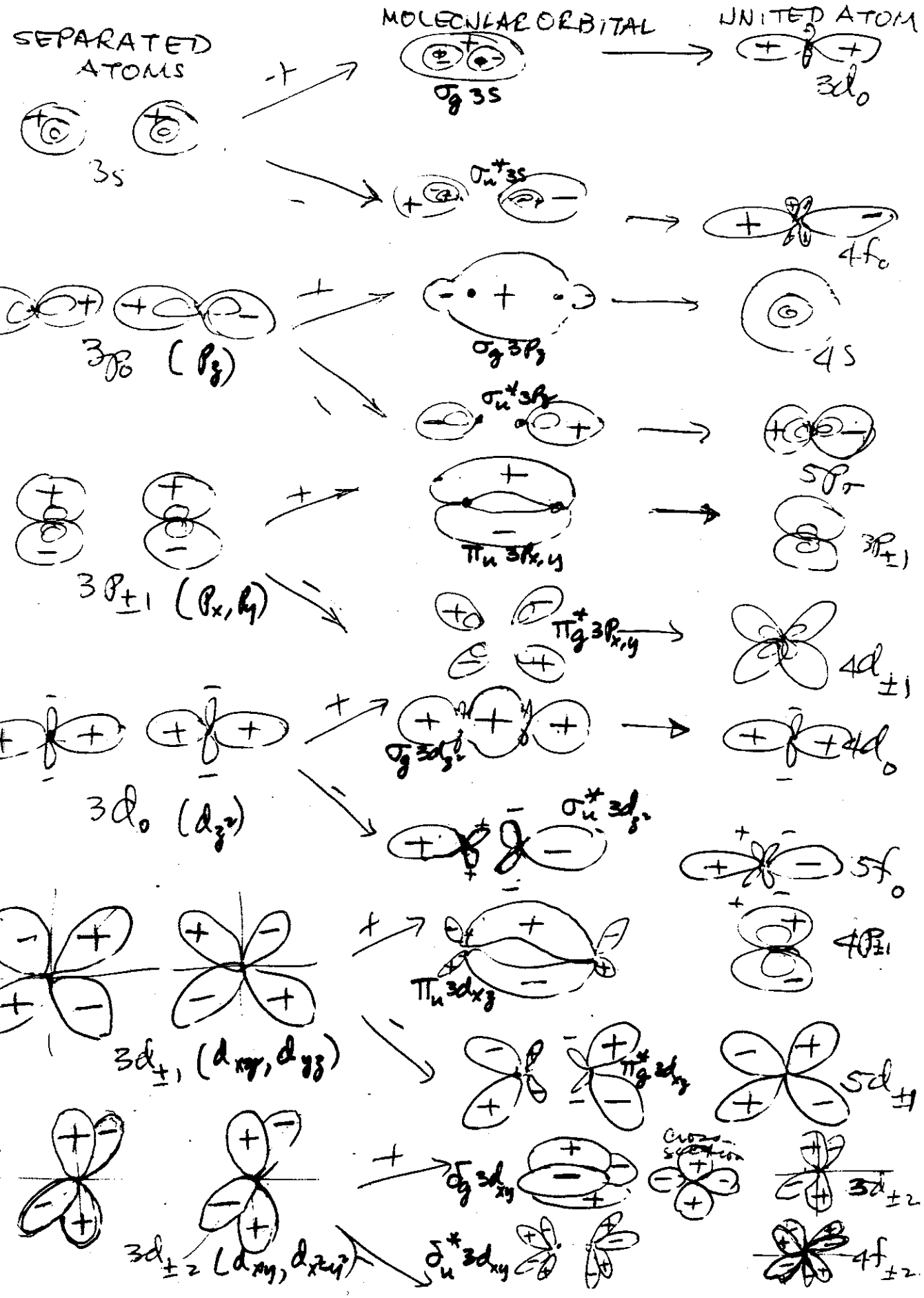
MOLECULAR ORBITAL

SEPARATED ATOMS

UNITED ATOM




SEPARATED ATOMS
MOLECULAR ORBITAL
UNITED ATOM
1S
σ_g 1S
σ_u^* 1S
1S
2P$_0$
2S
σ_g 2S
σ_u^* 2S
2S
3P$_0$
2P$_0$
σ_g 2P$_z$
σ_u^* 2P$_z$
3S
4P$_0$
2P$_{\pm 1}$
π_u 2P$_{x,y}$
π_g^* 2P$_{x,y}$
2P$_{\pm 1}$
3d$_{\pm 1}$


SEPARATED ATOMS
MOLECULAR ORBITAL
UNITED ATOM
3s
$\sigma_g 3s$
$3d_0$
$\sigma_u^* 3s$
$4f_0$
$3p_0$ (p_z)
$\sigma_g 3p_z$
4s
$\sigma_u^* 3p_z$
$5p_\sigma$
$3p_{\pm 1}$ (p_x, p_y)
$\pi_u 3p_{x,y}$
$3p_{\pm 1}$
$\pi_g^* 3p_{x,y}$
$4d_{\pm 1}$
$3d_0$ (d_{z^2})
$\sigma_g 3d_{z^2}$
$4d_0$
$\sigma_u^* 3d_{z^2}$
$5f_0$
$3d_{\pm 1}$ (d_{xy}, d_{yz})
$\pi_u 3d_{xz}$
$4p_{\pm 1}$
$\pi_g^* 3d_{xy}$
$5d_{\pm 1}$
$3d_{\pm 2}$ ($d_{xy}, d_{x^2-y^2}$)
$\delta_g 3d_{xy}$
Cross section
$3d_{\pm 2}$
$\delta_u^* 3d_{xy}$
$4f_{\pm 2}$

UNITED ATOM ATOMIC ORBITALS OF VARIOUS SYMMETRIES

	gerade $m_\ell=0$ σ_g	ungerade $m_\ell=0$ σ_u	gerade $\lvert m_\ell\rvert=1$ π_g	ungerade $\lvert m_\ell\rvert=1$ π_u	gerade $\lvert m_\ell\rvert=2$ δ_g	ungerade $\lvert m_\ell\rvert=2$ δ_u
	$1s$					
E	$2s$	$2p_0$		$2p_{\pm1}$		
N	$3s$	$3p_0$	$3d_{\pm1}$	$3p_{\pm1}$	$3d_{\pm2}$	
E	$3d_0$					
R	$4s$	$4p_0$	$4d_{\pm1}$	$4p_{\pm1}$	$4d_{\pm2}$	$4f_{\pm2}$
G	$4d_0$	$4f_0$		$4f_{\pm1}$		
Y	$5s$	$5p_0$	$5d_{\pm1}$	$5p_{\pm1}$	$5d_{\pm2}$	$5f_{\pm2}$
	$6s$	$5f_0$	$5g_{\pm1}$	$5f_{\pm1}$		
↓	$5d_0$	$6p_0$	$6d_{\pm1}$	$6p_{\pm1}$		
	$5g_0$	$6f_0$	$6g_{\pm1}$	$6f_{\pm1}$		
	$6d_0$	$6h_0$				

In constructing the correlation diagram for separated atoms → molecules → united atom, note that

1) Λ is conserved

s_σ or p_σ or d_σ	⟶	σ	⟶ any of s_σ, p_σ, d_σ etc.
SEPARATED ATOMS		M.O.	UNITED ATOM

(In the separated or united atoms, Λ corresponds to m_ℓ values, the angular momentum about the z axis.)

2) g or u symmetry is conserved

g (with respect to mid-point)	⟶	g	⟶ s, d, g etc. (gerade orbitals)
u	⟶	u	⟶ p, f, h, etc. (ungerade orbitals)
SEPARATED ATOMS		M.O.	UNITED ATOM

(The classification of the united atom atomic orbitals is summarized on the next page)

Since united atom s, d_σ, g_σ etc. can only be obtained from $\sigma_g ns$, $\sigma_g np_0$, $\sigma_g nd_0$, $\sigma_g nf_0$, etc. molecular orbitals, we need only to order these particular S.A. orbitals in increasing energy and, the U.A. orbitals also in increasing energy and connect them, as shown below:

1s + 1s	$\sigma_g 1s$	1s
2s + 2s	$\sigma_g 2s$	2s
$2p_0$ + $2p_0$	$\sigma_g 2p_0$	3s
3s + 3s	$\sigma_g 3s$	$3d_0$
$3p_0$ + $3p_0$	$\sigma_g 3p_0$	4s
$3d_0$ + $3d_0$	$\sigma_g 3d_0$	$4d_0$
4s + 4s	$\sigma_g 4s$	5s
$4p_0$ + $4p_0$	$\sigma_g 4p_0$	6s
SEPARATED ATOMS	M.O.	UNITED ATOM

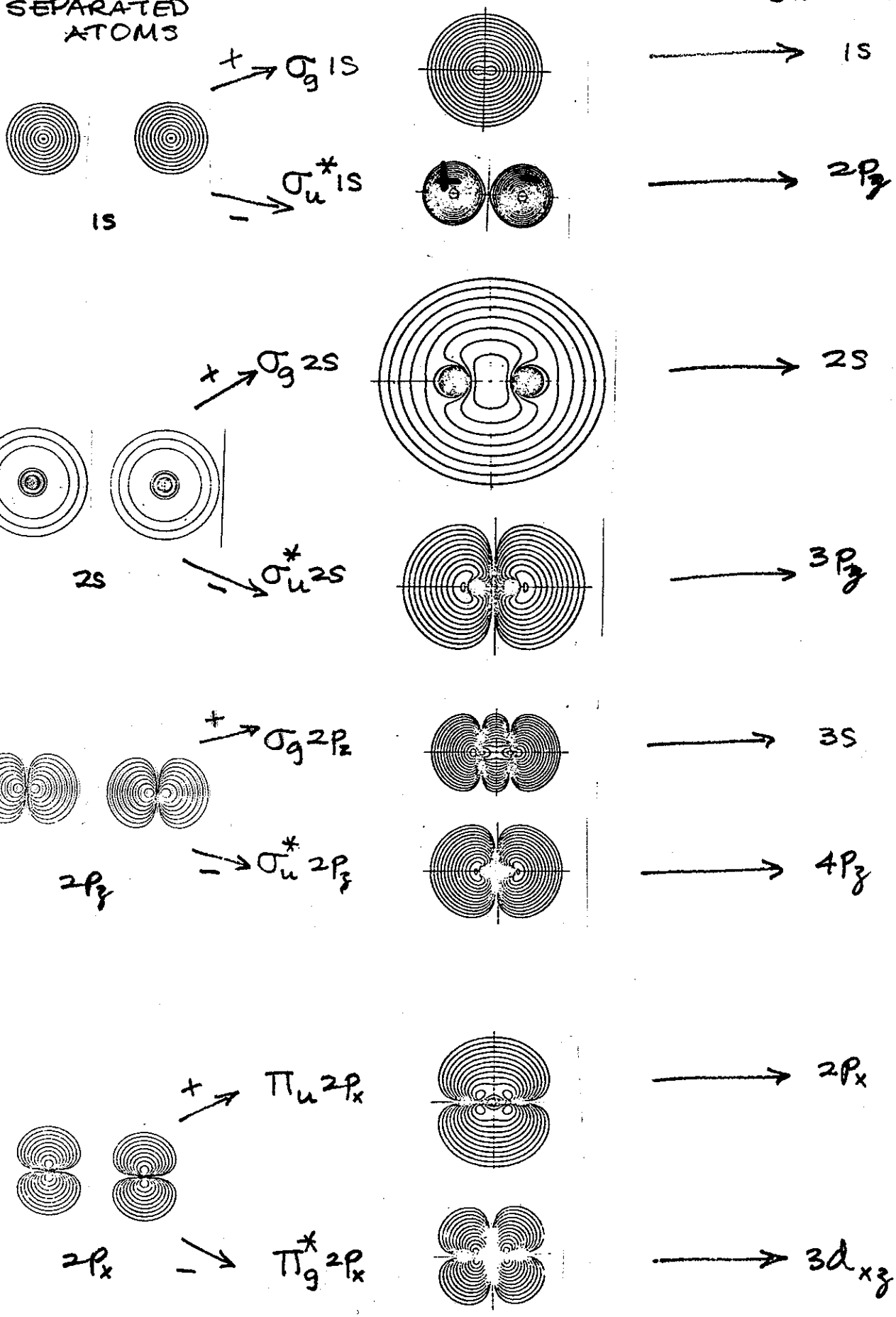
We can follow the same procedure for ungerade combinations of p_π, d_π, f_π etc. separated atom orbitals leading to p_π, f_π, h_π, etc. united atom orbitals. And so on for all the other combinations. This is how the correlations on the previous pages were obtained. Of course one can also determine the identity of the U.A. orbital from the contour diagrams in the limit of R→0. Note that if the S.A. atomic orbitals are arranged in their order of increasing energy, the connecting lines corresponding to M.O.'s of the same type (as in the above σ_g, or σ_u or π_g or π_u etc.) will never cross. Thus, the so-called "non-crossing rule" is automatically satisfied. Other correlations beyond the ones given in the previous drawings are given below:

SEPARATED ATOM	M.O.	UNITED ATOM
$4s + 4s$	$\sigma_g 4s$	$5s$
$4s - 4s$	$\sigma_u^* 4s$	$6p_0$
$4p_0 + 4p_0$	$\sigma_g 4p_z$	$6s$
$4p_0 - 4p_0$	$\sigma_u^* 4p_z$	$6f_0$
$4p_{\pm1} + 4p_{\pm1}$	$\pi_u 4p_{x,y}$	$4f_{\pm1}$
$4p_{\pm1} - 4p_{\pm1}$	$\pi_g^* 4p_{x,y}$	$5g_{\pm1}$
$4d_0 + 4d_0$	$\sigma_g 4d_{z^2}$	$5d_0$
$4d_0 - 4d_0$	$\sigma_u^* 4d_{z^2}$	$6h_0$
$4d_{\pm1} + 4d_{\pm1}$	$\pi_u 4d_{xy}$	$5p_{\pm1}$
$4d_{\pm1} - 4d_{\pm1}$	$\pi_g^* 4d_{xz}$	$4d_{\pm1}$
$4d_{\pm2} + 4d_{\pm2}$	$\delta_g 4d_{xy}$	$4d_{\pm2}$
$4d_{\pm2} - 4d_{\pm2}$	$\delta_u^* 4d_{xy}$	$5f_{\pm2}$

MOLECULAR ORBITAL

SEPARATED ATOMS

UNITED ATOM



MOLECULAR ORBITAL DESCRIPTION OF SOME DIATOMIC MOLECULES:

ELECTRONIC CONFIGURATIONS AND ELECTRON DENSITY CONTOURS

H_2 : $(\sigma_g 1s)^2$ in the Separated Atom notation

$(1\sigma_g)^2$ in the Symmetry notation

Li_2 : $(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2$

$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2$

B_2 : $(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\pi_u 2p)^2$

$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^2$

C_2 : $(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\pi_u 2p)^4$

$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4$

N_2 : $(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4$

$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4$

O_2 : $(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g^* 2p)^2$

$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4(1\pi_g)^2$

F_2 : $(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g^* 2p)^4$

$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4(1\pi_g)^4$

The electron density contours for each of the above MO's are shown on the following pages.

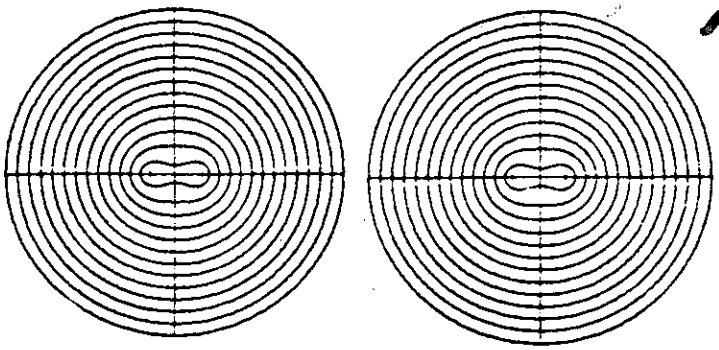


Fig. 1 (left). Hydrogen Molecule Total Electron Density Contours. Fig. 2 (right). Hydrogen Molecule 1 Sigma G Orbital Contours.

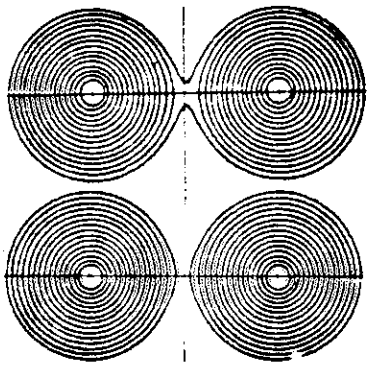


Fig. 4 (left). Lithium Molecule 1 Sigma G Orbital Contours.

Fig. 5 (left). Lithium Molecule 1 Sigma U Orbital Contours.

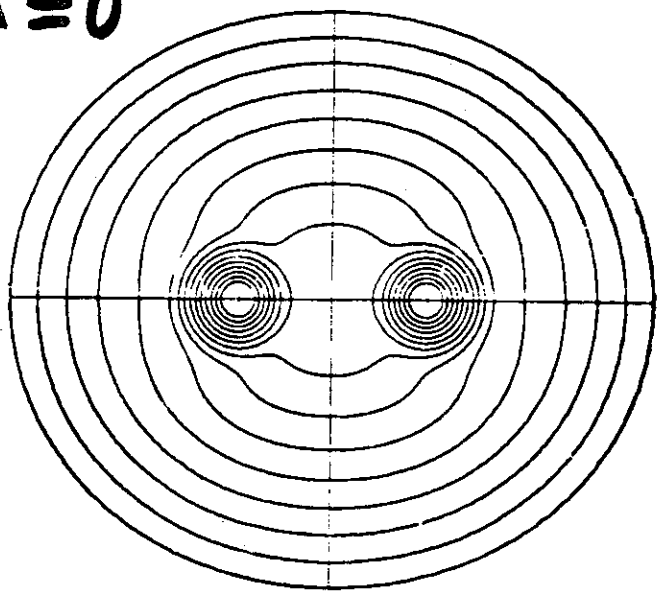


Fig. 3. Lithium Molecule Total Electron Density Contours.

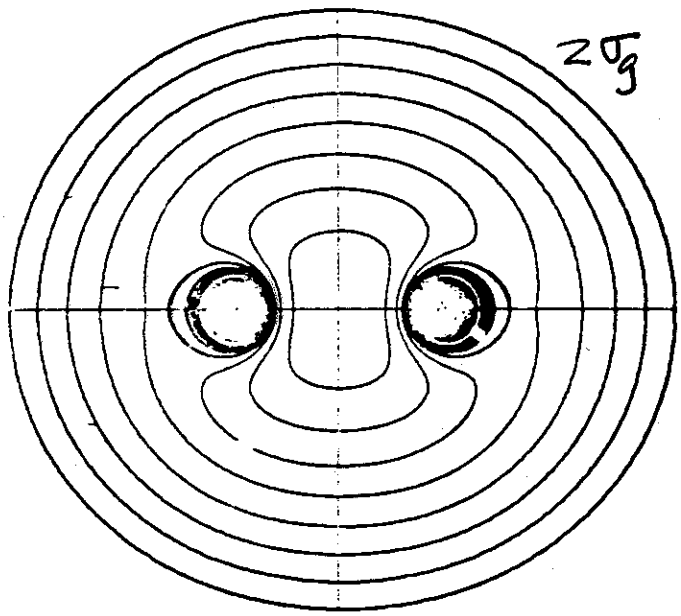


Fig. 6. Lithium Molecule 2 Sigma G Orbital Contours.

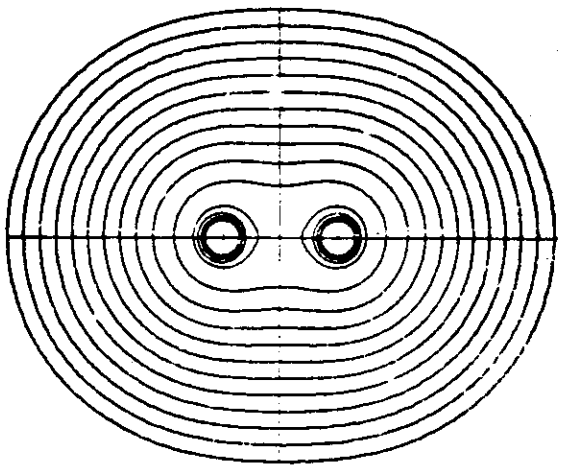
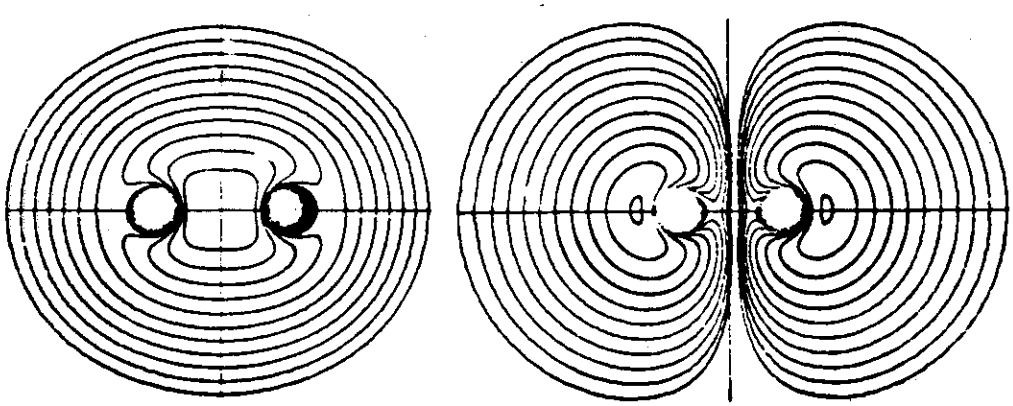


Fig. 7. Boron Molecule Total Electron Density Contours.

Fig. 8 (left). Boron Molecule 1 Sigma G Orbital Contours. Fig. 9 (right). Boron Molecule 1 Sigma U Orbital Contours.



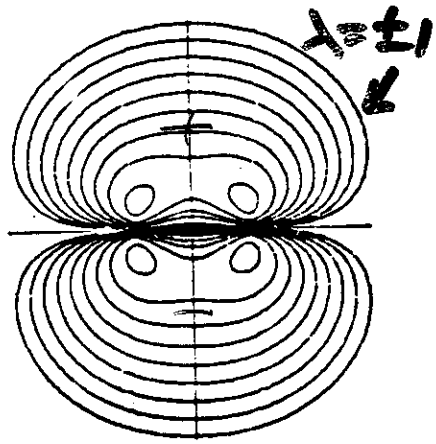


Fig. 10 (left). Boron Molecule 2 Sigma G Orbital Contours. Fig. 12 (right). Boron Molecule 1 Pi U Orbital Contours.

Fig. 11 (center). Boron Molecule 2 Sigma U Orbital Contours.

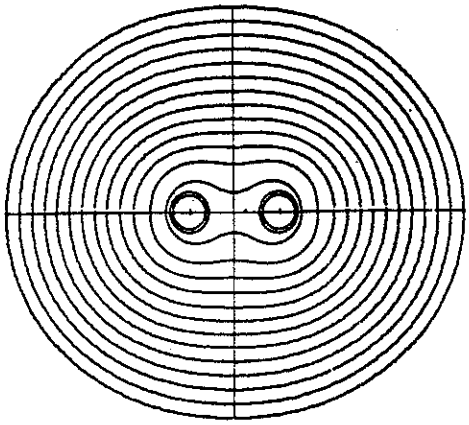


Fig. 13. Carbon Molecule Total Electron Density Contours.

Fig. 14 (left). Carbon 1 Sigma G Orbital Contours. Fig. 15 (right). Carbon Molecule 1 Sigma U Orbital Contours.

Fig. 20 (left). Nitrogen Molecule 1 Sigma G Orbital Contours. Fig. 21 (right). Nitrogen 1 Sigma U Orbital Contours.

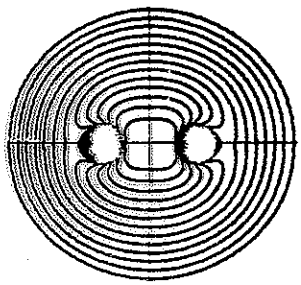


Fig. 22. Nitrogen 2 Sigma G Orbital Contours.

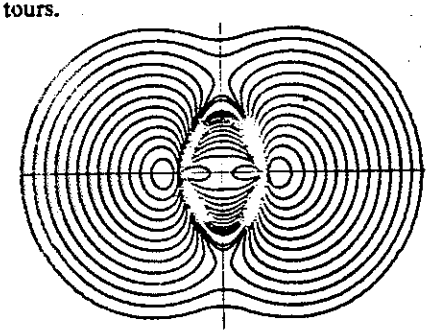
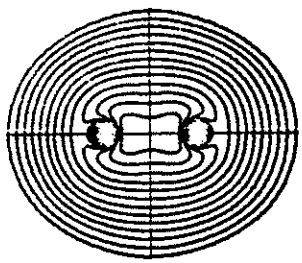


Fig. 25. Nitrogen 3 Sigma G Orbital Contours.



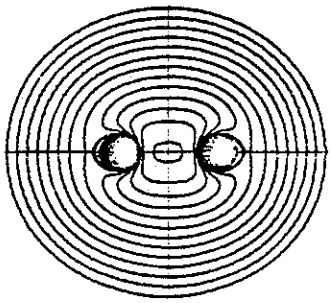


Fig. 16. Carbon Molecule 2 Sigma G Orbital Contours.

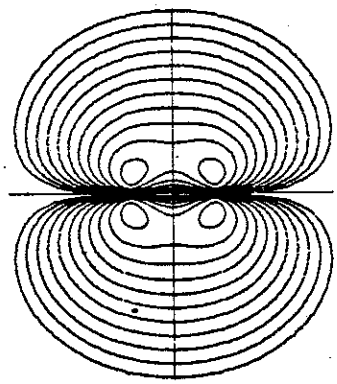


Fig. 18. Carbon Molecule 1 P1 U Orbital Contours.

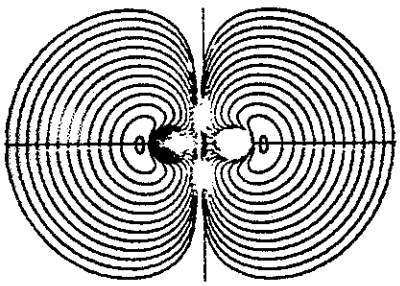


Fig. 23. Nitrogen 2 Sigma U Orbital Contours.

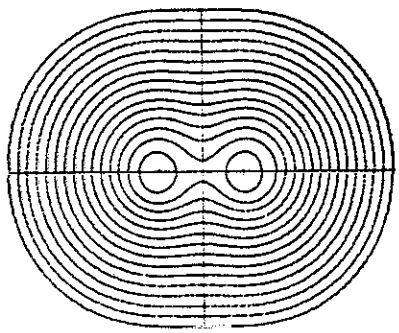
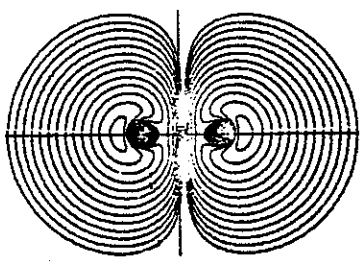


Fig. 26. Oxygen Molecule Total Electron Density Contours.



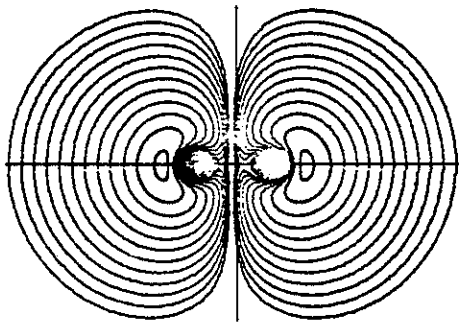


Fig. 17. Carbon Molecule 2 Sigma U Orbital Contours.

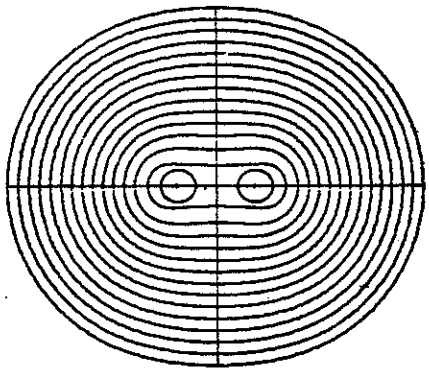


Fig. 19. Nitrogen Molecule Total Electron Density Contours.

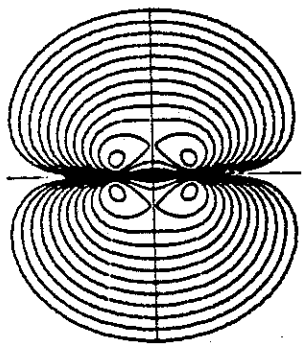


Fig. 24. Nitrogen 1 P1 U Orbital Contours.

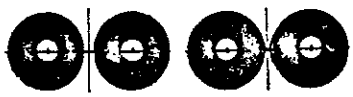


Fig. 27 (left). Oxygen Molecule 1 Sigma G Orbital Contours. Fig. 28 (right). Oxygen Molecule 1 Sigma U Orbital Contours.

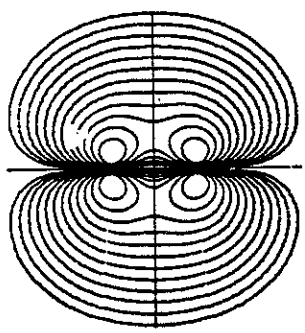


Fig. 29 (left). Oxygen Molecule 2 Sigma G Orbital Contours. Fig. 30 (center). Oxygen Molecule 2 Sigma U Orbital Contours. Fig. 31 (right). Oxygen Molecule 1 P1 U Orbital Contours.

Fig. 32. Oxygen Molecule 3 Sigma G Orbital Contours.

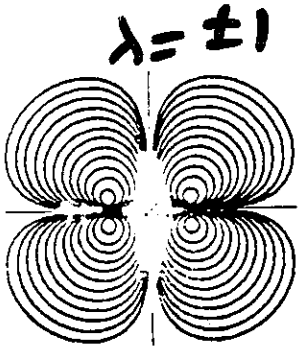


Fig. 33. Oxygen Molecule 1 PI G Orbital Contours.

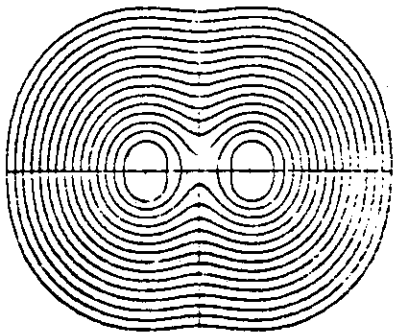


Fig. 34. Fluorine Molecule Total Electron Density Contours.

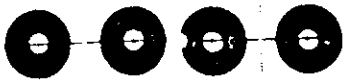


Fig. 35 (left). Fluorine Molecule 1 Sigma G Orbital Contours. Fig. 36 (right). Fluorine Molecule 1 Sigma U Orbital Contours.

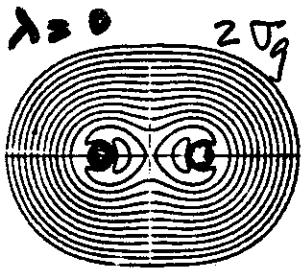


Fig. 37. Fluorine Molecule 2 Sigma G Orbital Contours.

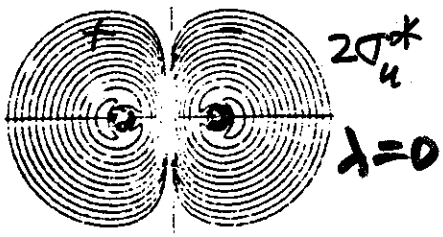


Fig. 38. Fluorine Molecule 2 Sigma U Orbital Contours.

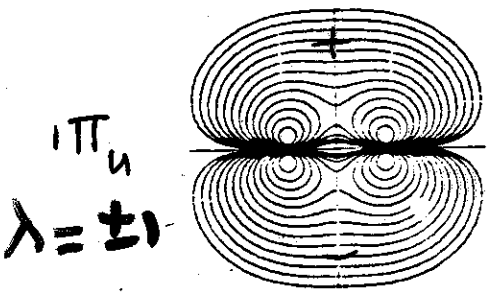


Fig. 39 (left). Fluorine Molecule 1 PI U Orbital Contours.

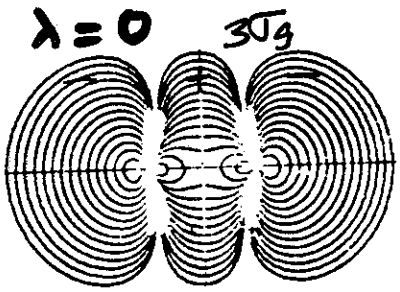


Fig. 40 (center). Fluorine Molecule 3 Sigma G Orbital Contours.

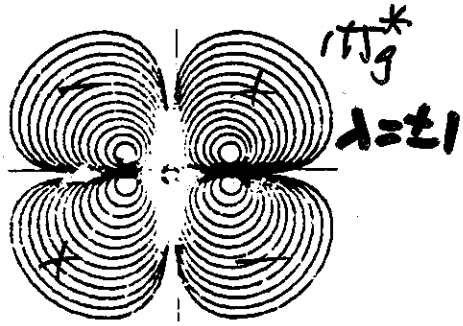
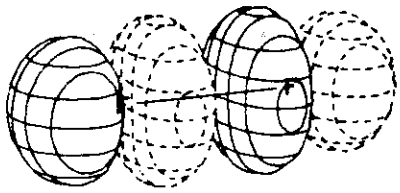


Fig. 41 (right). Fluorine Molecule 1 PI G Orbital Contours.

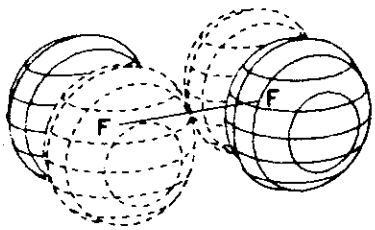
F_2 molecule

36. Fluorine

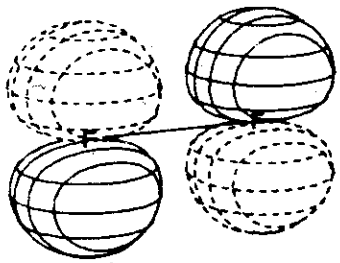
Symmetry: $D_{\infty h}$



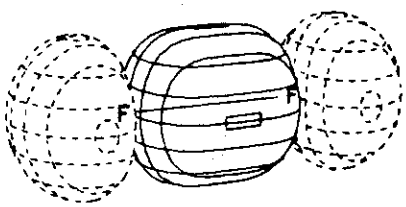
$3\sigma_u$ E= 0.3863



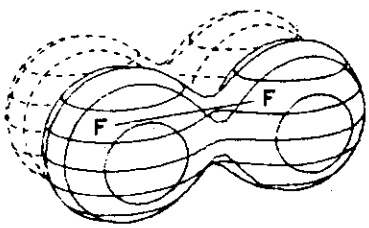
$1\pi_g^*$ E=-0.4318



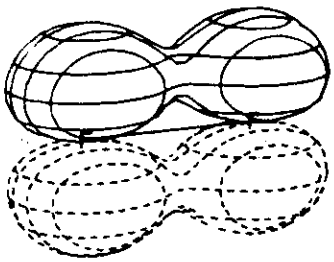
$1\pi_g^*$ E=-0.4318



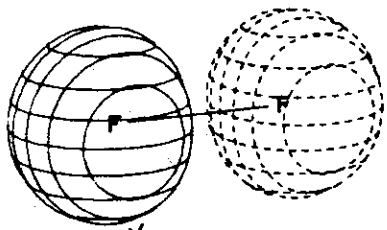
$3\sigma_g$ E=-0.5037



$1\pi_u$ E=-0.5645

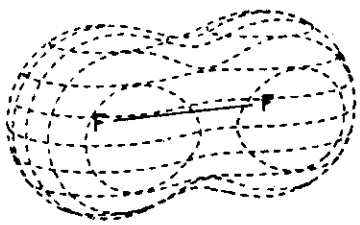


$1\pi_u$ E=-0.5645



$2\sigma_u^*$ E=-1.3173

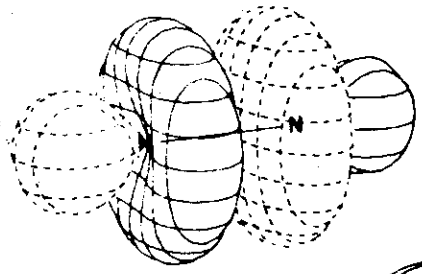
← dashed curves means negative values of wavefunction



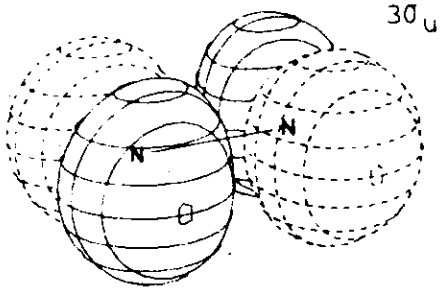
$2\sigma_g$ E=-1.5841

16. Nitrogen

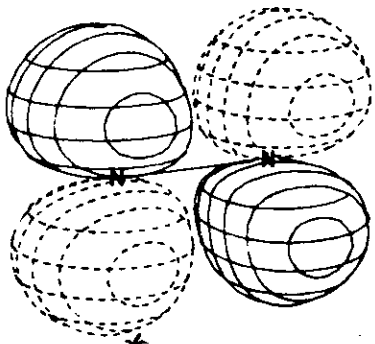
Symmetry: $D_{\infty h}$



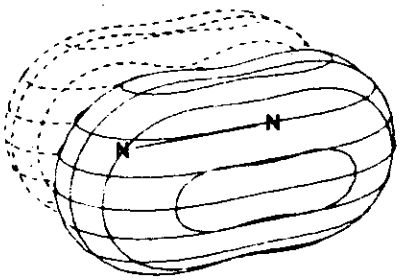
$3\sigma_u$ E= 1.2262



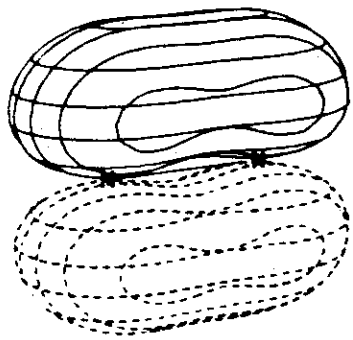
$1\pi_g^*$ E= 0.3002



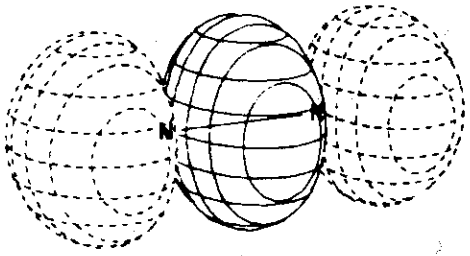
$1\pi_g^*$ E= 0.3002



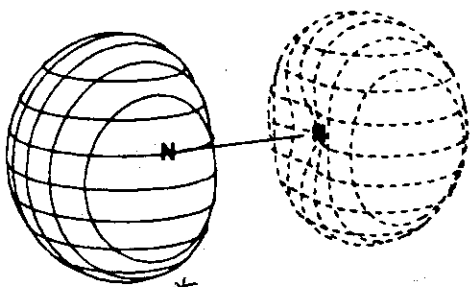
$1\pi_u$ E=-0.5454



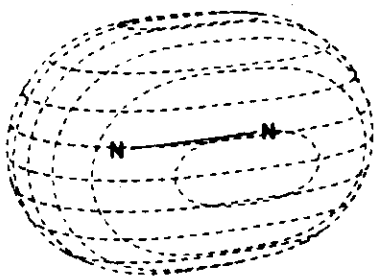
$1\pi_u$ E=-0.5454



$3\sigma_g$ E=-0.5555



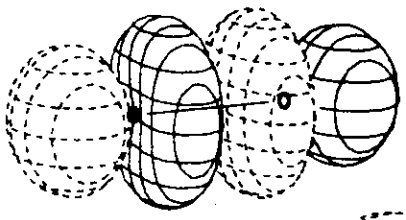
$2\sigma_u^*$ E=-0.7137



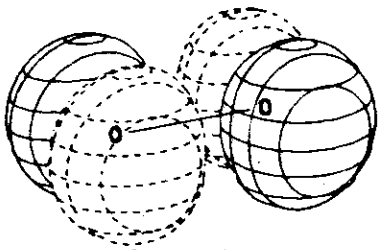
$2\sigma_g$ E=-1.4211

23. Oxygen (Triplet)

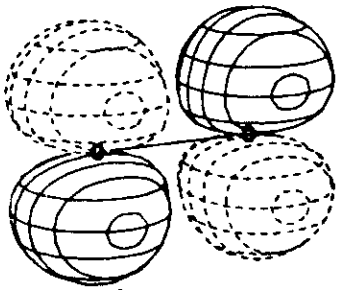
Symmetry: $D_{\infty h}$



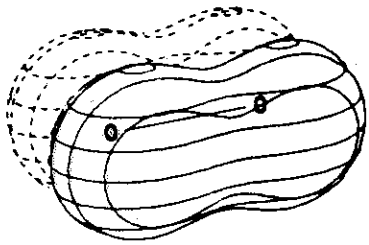
$3\sigma_u$



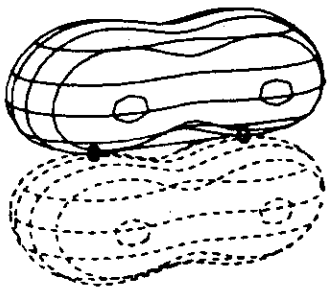
$1\pi_g^*$ E=-0.5319



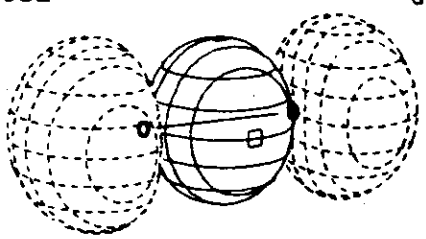
$1\pi_g^*$ E=-0.5319



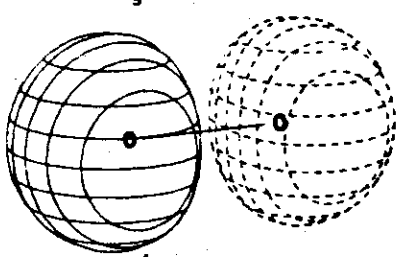
$1\pi_u$ E=-0.7052



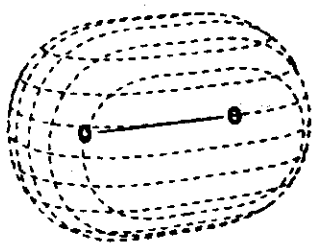
$1\pi_u$ E=-0.7052



$3\sigma_g$ E=-0.7357



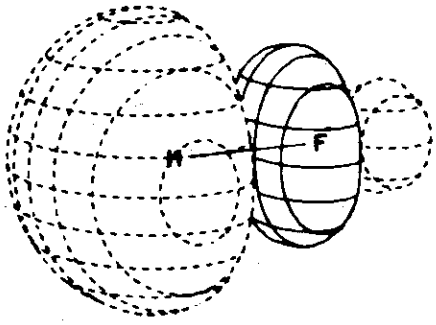
$2\sigma_u^*$ E=-1.0987



$2\sigma_g$ E=-1.6488

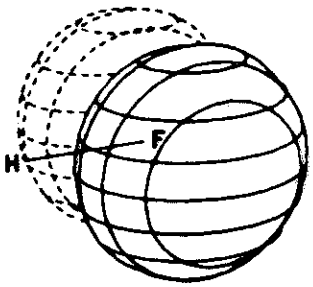
10. Hydrogen Fluoride

Symmetry: $C_{\infty v}$



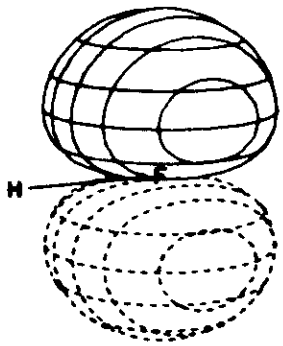
$\lambda = 0$

4σ E= 0.2906



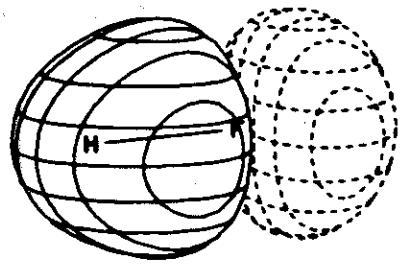
$\lambda = \pm 1$

1π E=-0.6505



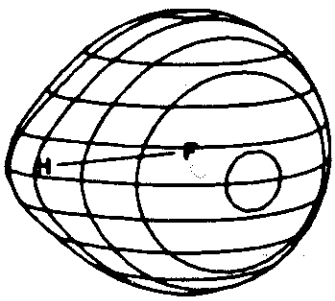
1π E=-0.6505

lone pairs on F



3σ E=-0.7685

$\lambda = 0$



2σ E=-1.6013

The attached figure is from a paper by R. F. W. Bader and K. E. Laidig, *J. Mol. Struct.* 261, 1-20 (1992).

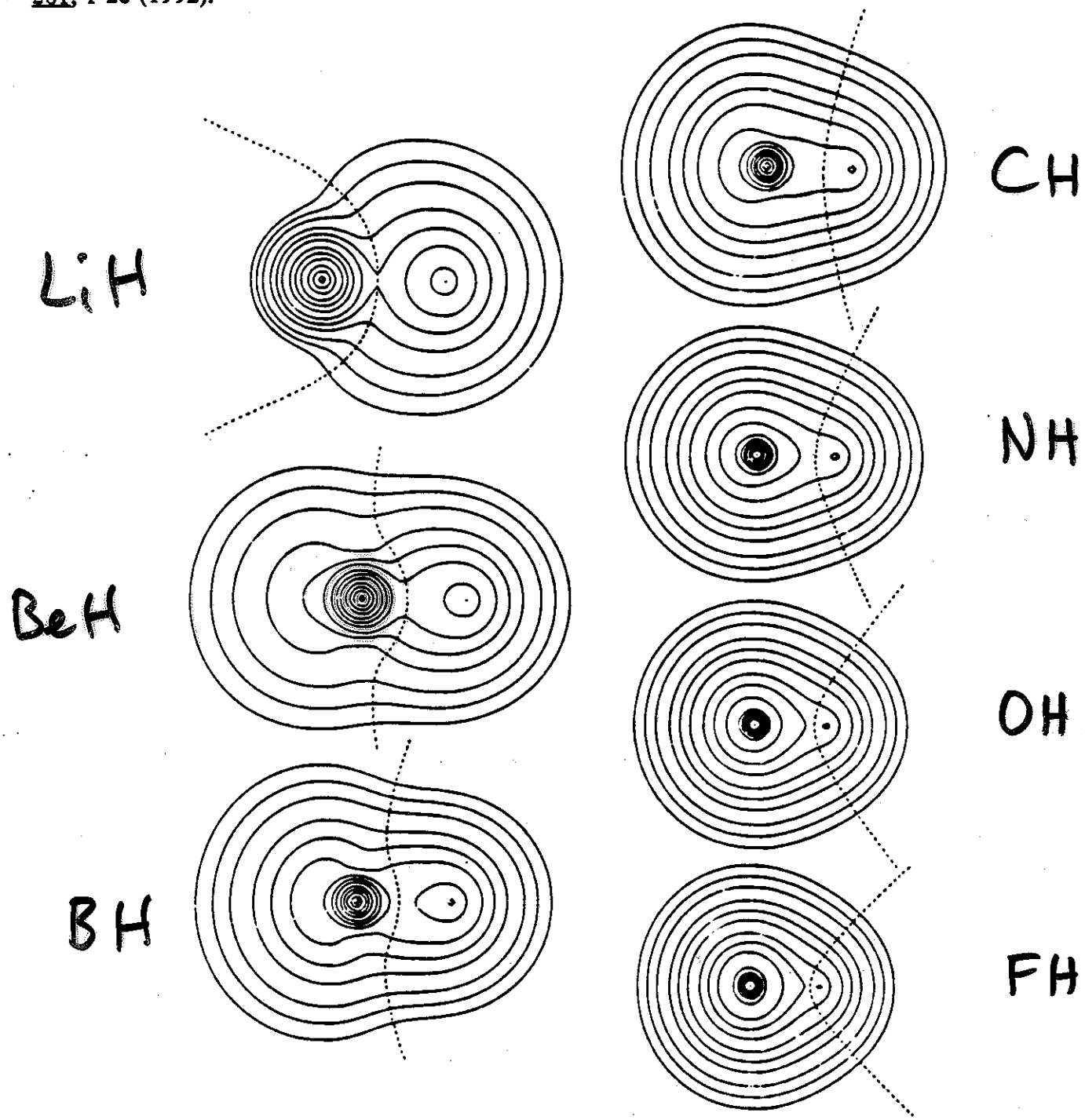
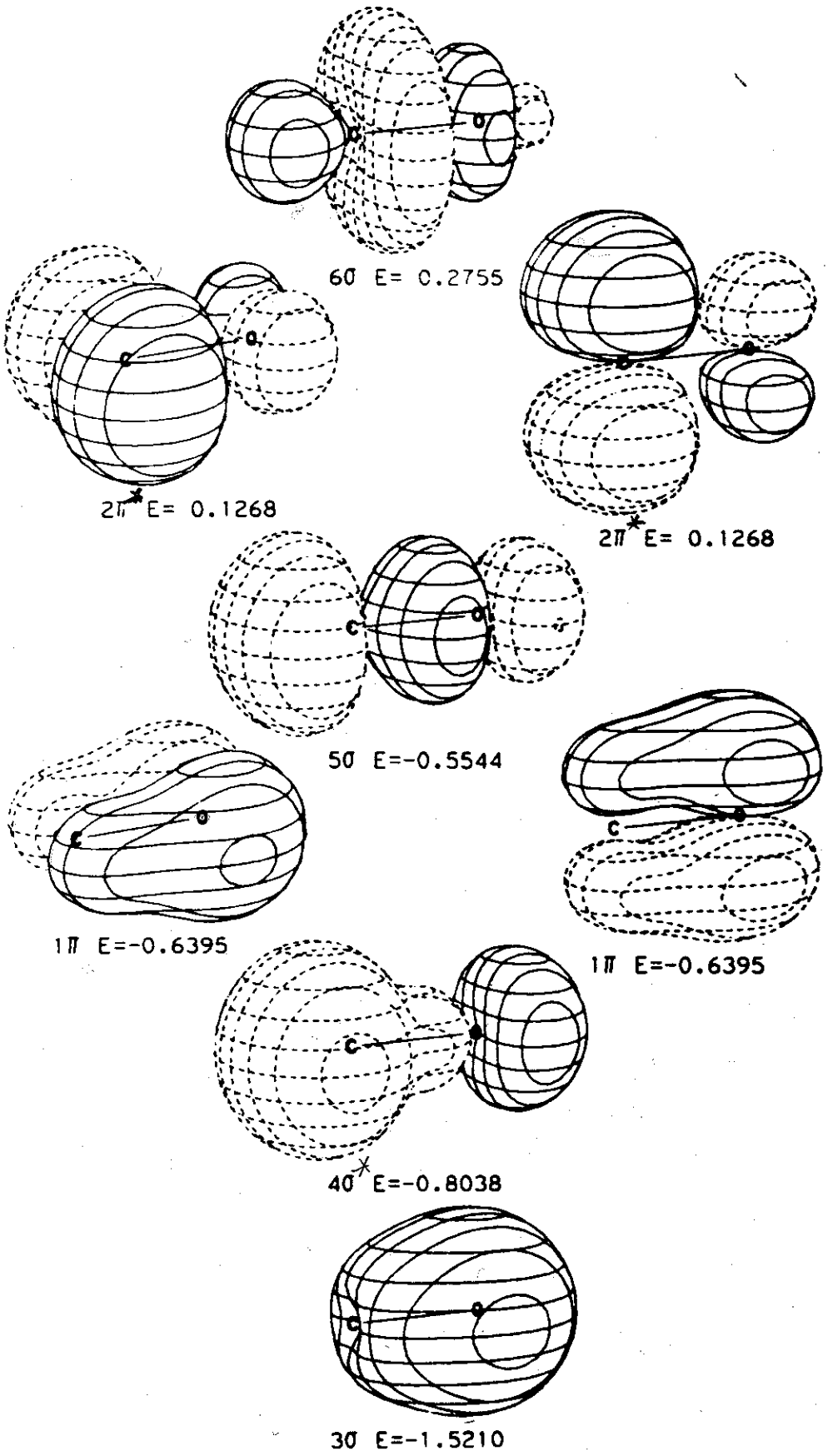


Fig. 1. Contour maps of the ground state electronic charge distributions of the hydrides: LiH, BeH and BH (left-hand side); CH, NH, OH and HF (right-hand side). Also shown are the atomic boundaries defined by the surfaces of zero flux in the gradient vector field of the charge density. The contours increase in value from the outermost contour inwards in steps of 2×10^n, 4×10^n and 8×10^n with n beginning at -3.

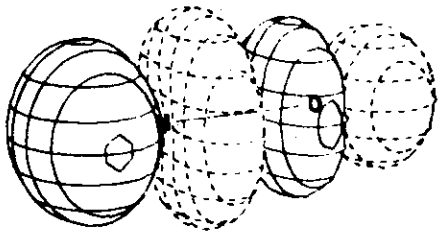
15. Carbon Monoxide

Symmetry: $C_{\infty v}$

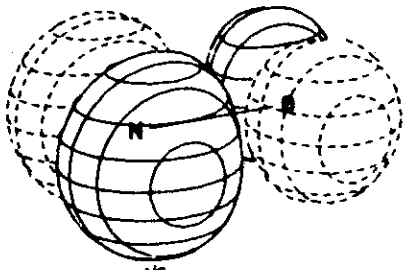


17. Nitric Oxide

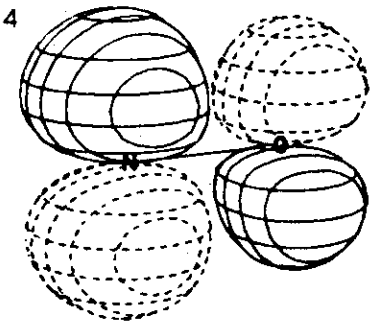
Symmetry: $C_{\infty v}$



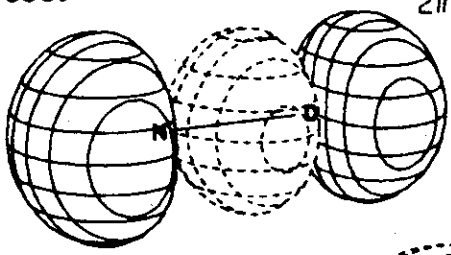
6σ E= 0.6864



2π* E=-0.3359

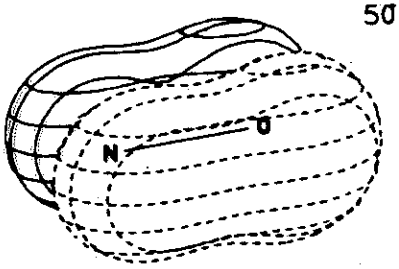


2π* E=-0.3359

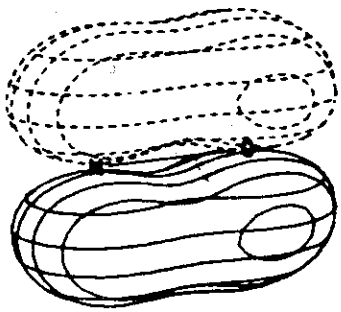


odd e⁻

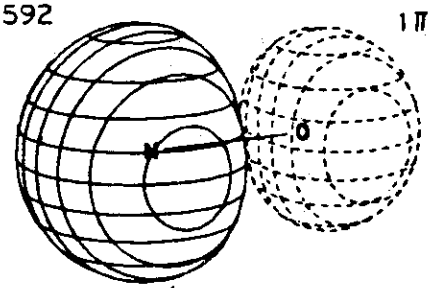
5σ E=-0.5371



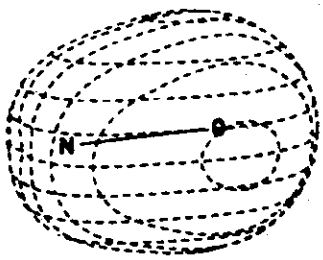
1π E=-0.5592



1π E=-0.5592



4σ* E=-0.8554



3σ E=-1.4825