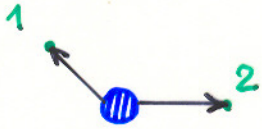
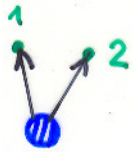
ELECTRON CORRELATION

He:





(V/A COULOMB INTERACTION)

COULOMB CORRELATION

ELECTRONS „AVOID" EACH OTHER
THEIR MOTION IS „CORRELATED"

THE MOST PREFERABLE POSITIONS OF TWO ELECTRONS

THIS EFFECT IS NOT DESCRIBED BY ANY THEORETICAL MODEL DEFINED WITHIN THE SINGLE CONFIGURATION APPROXIMATION

FERMI CORR. ⇒ (ONLY CORRELATION BETWEEN ELECTRONS WITH THE SAME PROJECTIONS OF SPIN IS INCLUDED DUE TO THE PROPERTIES OF SLATER DETERM.)

① $E_{corr} = E_{nrel} - E^{HF}$

„CORRELATION ENERGY"

RATHER ESTIMATED THAN EVALUATED

$< 1\%$ OF E_{TOTAL} !

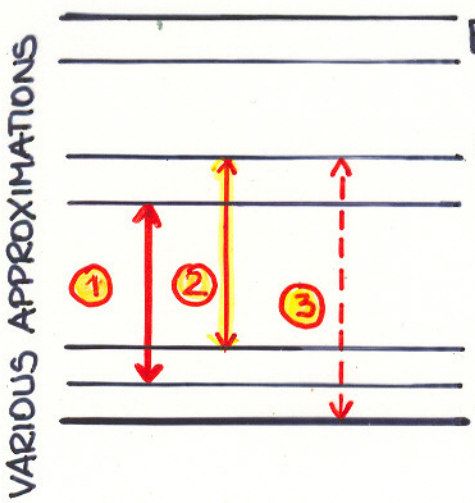
NON-RELATIVISTIC ENERGY, THE BEST FOR THE NON-RELATIVISTIC HAMILTONIAN

$H = \sum_i h(i) + \sum \frac{1}{r_{ij}}$

$E_{exp} - E_{nrel} = E_{rel}$

HARTREE-FOCK LIMIT: ENERGY OBTAINED FROM THE MODEL BASED ON SINGLE CONF. APPROXIMATION, DEFINED IN THE TERMS OF SINGLE PARTICLE APPROXIMATION

ERROR OF SCF



E^{SCF} IN ALGEBRAIC APPROXIMATION (LIMITED BASIS SET AND EXTENDED)

CLOSE TO THE HARTREE-FOCK LIMIT (PRACTICE)

E^{HF} – HARTREE-FOCK LIMIT (COMPLETE BASIS SET)

»FULL CI"

E_{nrel}

E_{exp}

② COMMON PRACTICE

③ „EXPERIMENTAL" CORRELATION ENERGY

HOW TO IMPROVE THE RESULTS OF SCF?

CORRELATION FACTORS } INTRODUCE THE DISTANCE r_{12}
CORRELATED FUNCTIONS } EXPLICITE INTO FUNCTION

He

$$\Psi = \varphi(1)\varphi(2)(1 + c\, r_{12})$$

↑ VARIATIONAL PARAMETER

FOR GREATER r_{12} => GREATER VALUES OF Ψ => GREATER $|\Psi|^2$ =>
BETTER DESCRIPTION OF ELECTRON CORRELATION

MORE ADVANCED

$$(1 + c_1 r_1^p + c_2 r_2^q + c_3 r_{12}^s)$$

c_1, c_2, c_3 – LINEAR VARIATIONAL PARAMETERS

p, q, s – VARIATIONAL PARAMETERS

1959 – C.I. PEKERIS : 1027 PARAMETERS => ENERGY OF He WITHIN THE ACCURACY OF 7 DIGITS, WITHIN THE ERROR OF EXPERIMENT ($\sim .1 cm^{-1}$).

THE SOLUTION OF NON-RELATIVISTIC EIGENVALUE PROBLEM FOR He IS KNOWN WITH THE ACCURACY OF 14 DIGITS.

HOW TO IMPROVE THE RESULTS OF SCF FOR $N > 2$ ELECTRON SYSTEMS?

MÖLLER-PLESSET PERTURBATION THEORY

$$H = \sum_i h(i) + \sum_{i<j} \frac{e^2}{r_{ij}} \qquad H\Psi = E\Psi$$

$$\sum_i F(i) = \sum_i h(i) + \sum_{q,i} \left(2\hat{J}_q(i) - \hat{K}_q(i)\right) \qquad F(i)\varphi_i = \varepsilon_i \varphi_i$$

$$H = \sum_i F(i) + \sum_{i<j} \frac{e^2}{r_{ij}} - \sum_i \sum_q \left(2J_q(i) - K_q(i)\right)$$

BEYOND H-F ↗ NON-CENTRAL PART OF COULOMB INT. RESPONSIBLE FOR ELECTRON CORREL.

$$H = \sum_i F(i) + \sum_{i<j} \frac{e^2}{r_{ij}} - \sum_i \sum_q \left(2J_q(i) - K_q(i)\right)$$

SMALL => PERTURBATION

$$H = H_0 + \lambda V$$

$$E^0 = \langle \psi^0 | H_0 | \psi^0 \rangle = \langle \psi^0 | \sum_i F(i) | \psi^0 \rangle \overset{\psi^0 \equiv \psi_{HF}}{=\!=} = \sum_i \varepsilon_i \quad \left(= \sum_i^{N/2} 2\varepsilon_p \right)$$

$$E^{(1)} = \langle \psi^0 | V | \psi^0 \rangle \overset{\psi^0 \equiv \psi_{HF}}{=\!=}$$

$$= \langle \psi^0 | \sum_{i<j} \frac{e^2}{r_{ij}} - \sum_i \sum_q \left(2J_q(i) - K_q(i)\right) | \psi^0 \rangle$$

+

$$E_{HF} = 2\sum_{p=1}^{N/2} \varepsilon_p - \sum_{p,q=1}^{N/2} \left(2J_{pq} - K_{pq}\right)$$

$E_{HF} = E^0 + E^{(1)}$ UP TO THE FIRST ORDER OF R-S PERTURBATION THEORY

↑ ENERGY FROM VARIATIONAL METHOD

$$E = E^0 + \lambda E^{(1)} + \lambda^2 E^{(2)} + \ldots$$

E_{HF} (SINGLE CONFIGURATION APPROXIMATION)

ELECTRON CORRELATION

BEYOND HARTREE-FOCK MODEL

EXCITED DETERMINANTS

HARTREE - FOCK PROCEDURE ⇒ K SPIN ORBITALS FOR N-ELECTRON SYSTEM

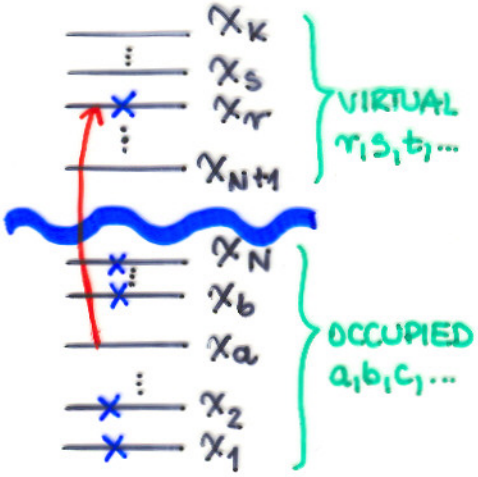
$$\binom{K}{N} = \frac{K!}{N!(K-N)!}$$

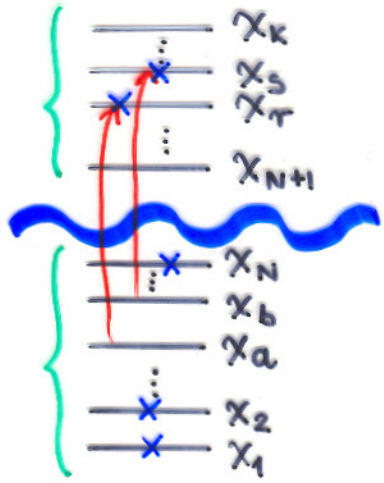
DETERMINANTS ONE OF WHICH DESCRIBES THE GROUND STATE WITHIN THE H-F MODEL

$|\Psi_0\rangle = |\chi_1, \chi_2, \ldots \chi_a, \chi_b, \ldots \chi_N\rangle$ REFERENCE STATE

$\chi_{N+1}, \ldots \chi_K$ – VIRTUAL STATES

CLASSIFICATION OF ALL THE OTHER DETERMINANTS BY HOW THEY DIFFER FROM THE REFERENCE STATE





$|\Psi_a^r\rangle = |\chi_1, \chi_2, \ldots \chi_r \chi_b \ldots \chi_N\rangle$

A SINGLY EXCITED DETERMINANT,

$|\Psi_{ab}^{rs}\rangle = |\chi_1, \chi_2, \ldots \chi_r, \chi_s, \ldots \chi_N\rangle$

DOUBLY EXCITED DETERMINANT

$\binom{K}{N}$ DETERMINANTS: HARTREE-FOCK GROUND STATE
SINGLY, DOUBLY, TRIPLY, QUADRUPLY...
... N-TUPLY EXCITED ...
CONFIGURATIONS

CI : CONFIGURATION INTERACTION

N-ELECTRON BASIS FUNCTIONS : EXCITED DETERMINANTS

$\{\chi_i\}$ - COMPLETE SET OF FUNCTIONS

$$\Phi(x_1) = \sum_i a_i \chi_i(x_1) \qquad \text{(EXACT)}$$

↖ EXPANSION COEFFICIENTS

$$\Phi(x_1 x_2) = \sum_i a_i(x_2)\, \chi_i(x_1)$$

↖ FUNCTIONS OF x_2

$$a_i(x_2) = \sum_j b_{ij} \chi_j(x_2)$$

$$\Phi(x_1 x_2) = \sum_{ij} b_{ij} \chi_i(x_1) \chi_j(x_2)$$

BUT

$$\Phi(x_1 x_2) = -\Phi(x_2 x_1) \Rightarrow \begin{cases} b_{ij} = -b_{ji} \\ b_{ii} = 0 \end{cases}$$

$$\Phi(x_1 x_2) = \sum_i \sum_{j<i} b_{ij} \left[\chi_i(x_1)\chi_j(x_2) - \chi_j(x_1)\chi_i(x_2) \right]$$

$$= \sum_{i<j} \sqrt{2}\, b_{ij} |\chi_i \chi_j| \qquad \text{SLATER DETERMINANT}$$

ARBITRARY ANTISYMMETRIC FUNCTION CAN BE EXACTLY EXPANDED IN TERMS OF DETERMINANTS FORMED FROM A COMPLETE SET OF ONE-PARTICLE (VARIABLE) FUNCTIONS

$\{\chi_i\}$ - COMPLETE SET OF SPIN-ORBITALS

REFERENCE H-F + SINGLY EXC. + DOUBLY EXC. + TRIPLY EXC. + ...

$$|\Phi\rangle = c_0 |\Psi_0\rangle + \sum_{ra} c_a^r |\Psi_a^r\rangle + \sum_{\substack{a<b \\ r<s}} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle + \sum_{\substack{a<b<c \\ r<s<t}} c_{abc}^{rst} |\Psi_{abc}^{rst}\rangle + \ldots$$

„CONFIGURATION INTERACTION"

$$\Phi_{CI} = c_0 |\Psi_0\rangle + c_S |S\rangle + c_D |D\rangle + c_T |T\rangle + c_Q |Q\rangle + \ldots$$

FULL CI:

EXACT EXPANSION:

$$\Phi = C_0\Psi_0 + \sum_{ar} C_a^r \Psi_a^r + \sum_{\substack{a<b \\ r<s}} C_{ab}^{rs} \Psi_{ab}^{rs} +$$

$$+ \sum_{\substack{a<b<c \\ r<s<t}} C_{abc}^{rst} \Psi_{abc}^{rst} + \sum_{\substack{a<b<c<d \\ r<s<t<u}} C_{abcd}^{rstu} \Psi_{abcd}^{rstu} + \dots$$

EACH DETERMINANT IS INCLUDED ONLY ONCE

ONLY COEFFICIENTS ARE UNKNOWN

$E_{CORR} = E_{FULL\,CI} - E_{HF}$ (NEGATIVE SINCE E_{HF} IS ALWAYS AN UPPER BOUND TO THE EXACT ENERGY).

↑ EXACT VALUE

$\langle\Phi|H|\Phi\rangle$ – MATRIX REPRESENTATION OF THE HAMILTONIAN IN THE BASIS OF N-ELECTRON FUNCTIONS

⇓ FULL CI MATRIX ⇒ EIGENVALUES

THE LOWEST = APPROXIMATION TO THE GROUND STATE ENERGY OF THE SYSTEM

THE HIGHER VALUES = EXCITED STATES

VARIATIONAL PRINCIPLE:

$c_0, c_a^r, c_{ab}^{rs}) \dots$ LINEAR VARIATIONAL PARAMETERS

$$\min\{E(c_0, c_a^r, \dots)\} \Rightarrow \sum_l C_l (H_{kl} - ES_{kl}) = 0$$

↑ UNKNOWN

FOR Φ_{FCI} – THE BEST ENERGY ONE CAN GET FOR A GIVEN ONE ELECTRON BASIS SET

	Ψ_0	$\lvert S\rangle$	$\lvert D\rangle$	$\lvert T\rangle$	$\lvert Q\rangle$ ...
$\langle\Psi_0\rvert$	$\langle\Psi_0\lvert H\rvert\Psi_0\rangle$	0	$\langle\Psi_0\lvert H\rvert D\rangle$	0	0 ...
$\langle S\rvert$		$\langle S\lvert H\rvert S\rangle$	$\langle S\lvert H\rvert D\rangle$	$\langle S\lvert H\rvert T\rangle$	0 ...
$\langle D\rvert$			$\langle D\lvert H\rvert D\rangle$	$\langle D\lvert H\rvert T\rangle$	$\langle D\lvert H\rvert Q\rangle$ ...
$\langle T\rvert$				$\langle T\lvert H\rvert T\rangle$	$\langle T\lvert H\rvert Q\rangle$ ...
$\langle Q\rvert$					$\langle Q\lvert H\rvert Q\rangle$
$\vdots$					

FULL CI MATRIX

1. THERE IS NO COUPLING BETWEEN HF GROUND Ψ_0 AND SINGLE EXCITATIONS $\langle\Psi_0|H|S\rangle=0$ (BUT THEY DO MIX INDIRECTLY)

BRILLOUIN'S THEOREM (VALID FOR THE GROUND STATE ONLY)

$$\langle\Psi_0|H|\Psi_a^r\rangle = \langle a|h|r\rangle + \sum_b \langle ab||rb\rangle$$

$$= \langle a|F|r\rangle = \varepsilon_{ar} = 0$$ WHEN H-F EQUATIONS ARE SOLVED

THERE IS NO DIRECT CONTRIBUTION TO THE ENERGY OF THE GROUND STATE DUE TO SINGLE EXCITATIONS (IF VIRTUAL SOLUTIONS ARE USED TO BUILD SINGLY EXCITED CONFIGURATION)

2. THERE IS NO COUPLING BETWEEN Ψ_0 AND TRIPLETS AND QUADRUPLES; WHY?

BUT $\langle D|H|Q\rangle \neq 0$ IF: $\langle\Psi_{ab}^{rs}|H|\Psi_{abcd}^{rstu}\rangle$ $\{a,b\}\in\{abcd\}$ $\wedge$ $\{rs\}\in\{rstu\}$

3. SINGLE EXCITATIONS CONTRIBUTE TO THE ENERGY INDIRECTLY, AND THEIR ROLE IS NEGLIGIBLE IN THE DESCRIPTION OF ENERGY

BUT THEY ARE VERY IMPORTANT FOR A PROPER DESCRIPTION OF ONE-ELECTRON PROPERTIES SUCH AS THE DIPOLE MOMENT

4. IT IS EXPECTED THAT THE DOUBLE EXCITATIONS ARE THE MOST IMPORTANT SINCE THEY MIX DIRECTLY WITH Ψ_0

5. CALCULATIONS ARE PERFORMED USING SPIN-ADAPTED CONFIGURATIONS (FUNCTIONS OF GOOD SYMMETRY : $\hat{S}^2$).

COMMON APPROXIMATIONS TO FCI:

1. FULL CI IN RESTRICTED SPACE

- ONLY TREAT VALENCE ELECTRONS
- ONLY INCLUDE ACTIVE ELECTRONS
- DISCARD VIRTUAL ORBITALS WITH VERY HIGH ENERGY:

CAS-CI = COMPLETE ACTIVE SPACE CI

2. TRUNCATION OF THE CI WAVEFUNCTION EXPANSION

CISD, CISDT, CISDTQ

$$|\Psi_{CISD}\rangle = a_0|\Phi_0\rangle + a_S|S\rangle + a_D|D\rangle$$

THE SIZE OF A PROBLEM GROWS FAST WITH THE SIZE OF A SYSTEM

CANONICAL HARTREE-FOCK ORBITALS ARE NOT THE BEST BASIS FOR CI CALCULATIONS: SLOW CONVERGENCE OF THE EXPANSION
LONG EXPANSIONS ...

WHICH FUNCTIONS TO USE IN ORDER TO AVOID THESE PROBLEMS?

HOW TO OBTAIN THE BEST POSSIBLE RESULT? FROM THE VARIATIONAL PRINCIPLE IT IS CLEAR THAT THE BEST FUNCTIONS HAVE TO MINIMIZE THE ENERGY:

MCHF (MC SCF)

MULTICONFIGURATION HARTREE-FOCK

BEYOND SINGLE CONFIGURATION APPROXIMATION!

1°. TRUNCATED CI EXPANSION

$$|\Psi_{MCHF}\rangle = \sum_I C_I |I\rangle$$

2°. BOTH: EXPANSION COEFFICIENTS AND ORTHONORMAL ORBITALS OF $|I\rangle$ ARE OPTIMIZED!

EXAMPLES:

He : $1s^2\ {}^1S$

NUMBER OF CONF.	E_{CI} (a.u.)	$\Delta = E_{exc} - E_{CI}$
1 (HF)	-2.8617	-0.0421
20	-2.9028	-0.0009
35	-2.9032	-0.0005
E_{exc}	-2.9037	

Be

$1s^2\,2s^2$ (H-F) -14.573

$1s^2\,2s^2$, $1s^2\,2p^2$ } CI -14.617 $C_1 = 0.95$

47% E_{corr} $C_2 = 0.31$

55 CONFIG. -14.661

$\Phi = \sum_i^{55} C_i \varphi_i$

94% E_{corr}

E_{exc} -14.667

TABLE 4-3 Convergence of an MCHF procedure for $1s^2\ {}^1S$ of He[a]

— DOUBLY EXCITED CONFIGURATIONS
— CONFIGURATIONS OF THE SAME PARITY

m	Configuration	E_{total}	ΔE_{nl} $n=2$	$n=3$	$n=4$	$n=5$
1	$1s^2$ (H-F)	−2.861680				
2	$+2s^2$	−2.877997	−0.016317			
3	$+3s^2$	−2.878871		−0.000874		
4	$+4s^2$	−2.878990			−0.000119	
5	$+2p^2$	−2.898554	−0.019564			
6	$+3p^2$	−2.900150		−0.001599		
7	$+4p^2$	−2.900399			−0.000249	
8	$+3d^2$	−2.902179		−0.001780		
9	$+4d^2$	−2.902523			−0.000344	
10	$+4f^2$	−2.902909			−0.000386	
11	$+5g^2$	−2.903033				−0.000124
E^{exact}		−2.903724				
$E-E^{\text{exact}}$		0.000691				

MC HF EXCITED CONFIGURATIONS

$\Delta E_{nl}(\max)$ FOR $l=m-1$

[a] C. Froese Fischer, *J. Comput. Phys.* **13**, 502 (1973).

85.10

TABLE 4-4 Mixing coefficients c_{nl} for $1s^2\,{}^1S$ of H^-, He, Li^+ and the 11-configuration MCHF approximation

	c_{nl}		
Configuration	H^-	He	Li^+
$1s^2$ H-F ⇒ MCHF:	0.972064	0.995967[a]	0.998354[b]
$2s^2$	−0.204931	−0.061750	−0.036953
$3s^2$	−0.013851	−0.007847	−0.005200
$4s^2$	−0.002458	−0.001707	−0.001198
$2p^2$	0.110658	0.062046	0.041604
$3p^2$	0.015753	0.011044	0.007793
$4p^2$	0.003553	0.002691	0.001978
$3d^2$	−0.018226	−0.012793	−0.009070
$4d^2$	−0.004747	−0.003467	−0.002520
$4f^2$	0.005508	0.004103	0.002980
$5g^2$	−0.002487	−0.001894	−0.001374
E^{HF}	−0.487927	−2.861680 H-F	−7.236415
E^{MCHF}	−0.527510	−2.903033 MCHF	−7.279017
E^{exact} [c]	−0.527751	−2.903724 exact	−7.279913
$E^{MCHF} - E^{exact}$	0.000241	0.000691	0.000906
% correlation	99.4%	98.4%	97.9%

INSTEAD OF VIRTUAL SOLUTIONS OF H-F ⇒ APPLY THESE ORBITALS (MCHF) TO BUILD THE CI EXPANSION!

B5.11

[a] C. Froese Fischer, *J. Comput. Phys.* **13**, 502 (1973).
[b] C. Froese Fischer, *Int. J. Quantum Chem.* **9**, 273 (1975).
[c] C. L. Pekeris, *Phys. Rev.* **112**, 1649 (1958).

PHYSICA SCRIPTA 28, 45 (1983).

Table II. *Expansion coefficients for some states in Be I* $\psi(\alpha LS) = c_1\Phi(\alpha LS) + c_2\Phi(\alpha_2) + c_3\Phi(\alpha_3) + \ldots$ *where* $|c_2| > |c_3| > \ldots$

αLS	α_2	α_3	α_4	c_1	c_2	c_3	c_4
e $2s2p_1^2\ ^1P$ $2s2p_1^2$	$2p_1^3 3d_2$ $2p_1^2 3d_2$	$2s3d_1^2$ $2s3d_1^2$	$2s3p_1^2$ $2s3p_1^2$	0.994	−0.069	0.054	−0.052
o $2p^3\ ^1S^o$ $2p^3$	$2p^3d^2$ $2p3d^2$	$2p3p^2$ $2p3p^2$		0.991	0.095	0.094	
$2s2p3p\ ^1P$	$2s2p^2$	$2p3p(^4D)3d$	$3s2p^2$	0.989	0.093	−0.063	−0.060
$2p^33p\ ^1S^o$	$2p^2$	$3p3d^2$		0.987	0.140	0.053	
$2s2p4p\ ^1P$	$2s2p^2$	$2p4p(^4P)3d$	$2s4p^2$	0.989	0.115	−0.073	−0.058
$2p^34p\ ^1S^o$	$2p^2$	$4p3d^2$		0.990	0.114	0.053	
$2s3s2p_1\ ^1P^o$	$2p_1^2 3p_2$	$3s2p_1 3d$		0.992	0.096	0.070	
$2p^23p\ ^1D^o$	$2p3p^2$	$2p3p(^4D)4p$	$3p3d^2$	0.990	0.098	0.061	0.054
$2p^24p\ ^1D^o$	$2p3p(^4P)4p$	$2p4p^2$	$4p3d^2$	0.989	0.097	0.084	0.054

Table III. *Wavelengths, f-values in the length* (f_l) *and velocity form* (f_v), *and transition probabilities (in* $10^8\ s^{-1}$) *for some transitions in Be I* ($\bar{f}$ – *without 1s excitation,* f – *with 1s excitation*)

Transition		λ(Å)	$\bar{f}_l$		$\bar{f}_v$		f_l		f_v	A ($10^8\ s^{-1}$)
ELECTRIC DIPOLE TRANSITIONS										
$2s2p^2\ ^1P$	$2p^3\ ^1S^o$	1901	0.1801	?	0.1863	?	0.1792	?	0.1797	0.0997
$2s2p^2\ ^1P$	$2s2p3s\ ^1P^o$	1906	0.0952		0.1010		0.0952		0.1110	0.0175
$2s2p3p\ ^1P$	$2p^23p\ ^1S^o$	2252	0.0919		0.0977		0.0913		0.0915	0.0363
$2s2p4p\ ^1P$	$2p^24p\ ^1S^o$	2285	0.0723		0.0920		0.0718		0.0860	0.0277
$2s2p4p\ ^1P$	$2p^24p\ ^1D^o$	2330	0.1063		0.1164		0.1066		0.1281	0.0078
$2s2p3p\ ^1P$	$2p^23p\ ^1D^o$	2378	0.0477		0.1157		0.0477		0.1273	0.0034

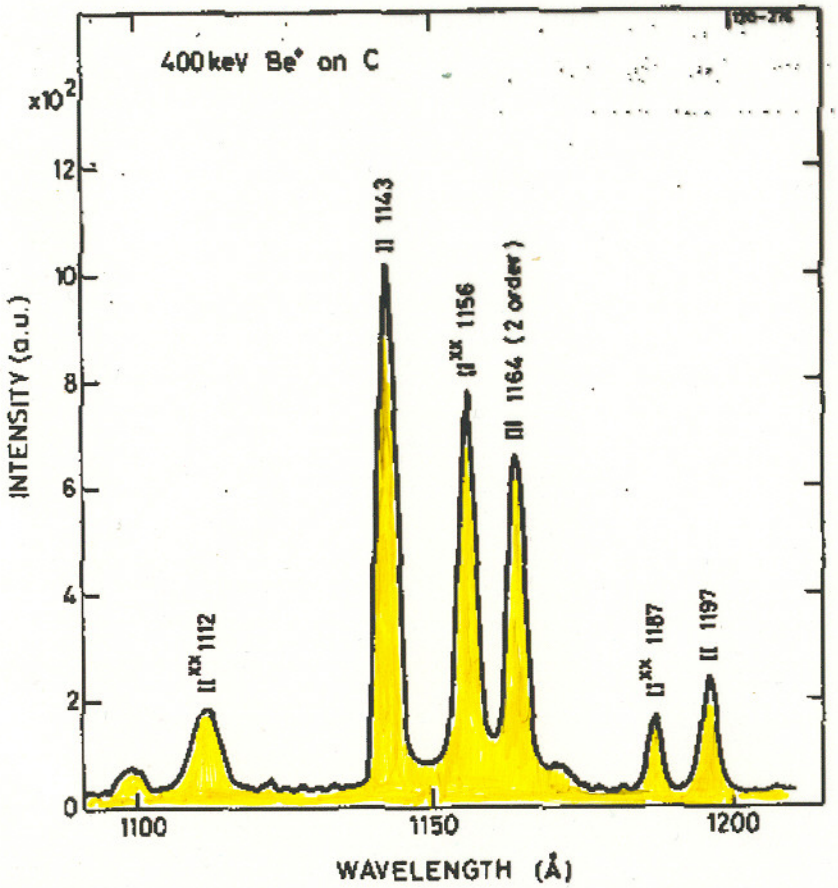


Fig. 1. The spectral region 1100–1200 A for 400 keV Be^+–C foil excitation.

$2p^2\ {}^1D$–$3p^2\ {}^1D$. In the wave-function expansion for $2p({}^1P)3p\ {}^2D$ reported in Table VI, we see that the $3p^2$ and $2p^2$ components are indeed nearly equal in magnitude although opposite in sign. Thus the stationary condition of the multiconfiguration wave

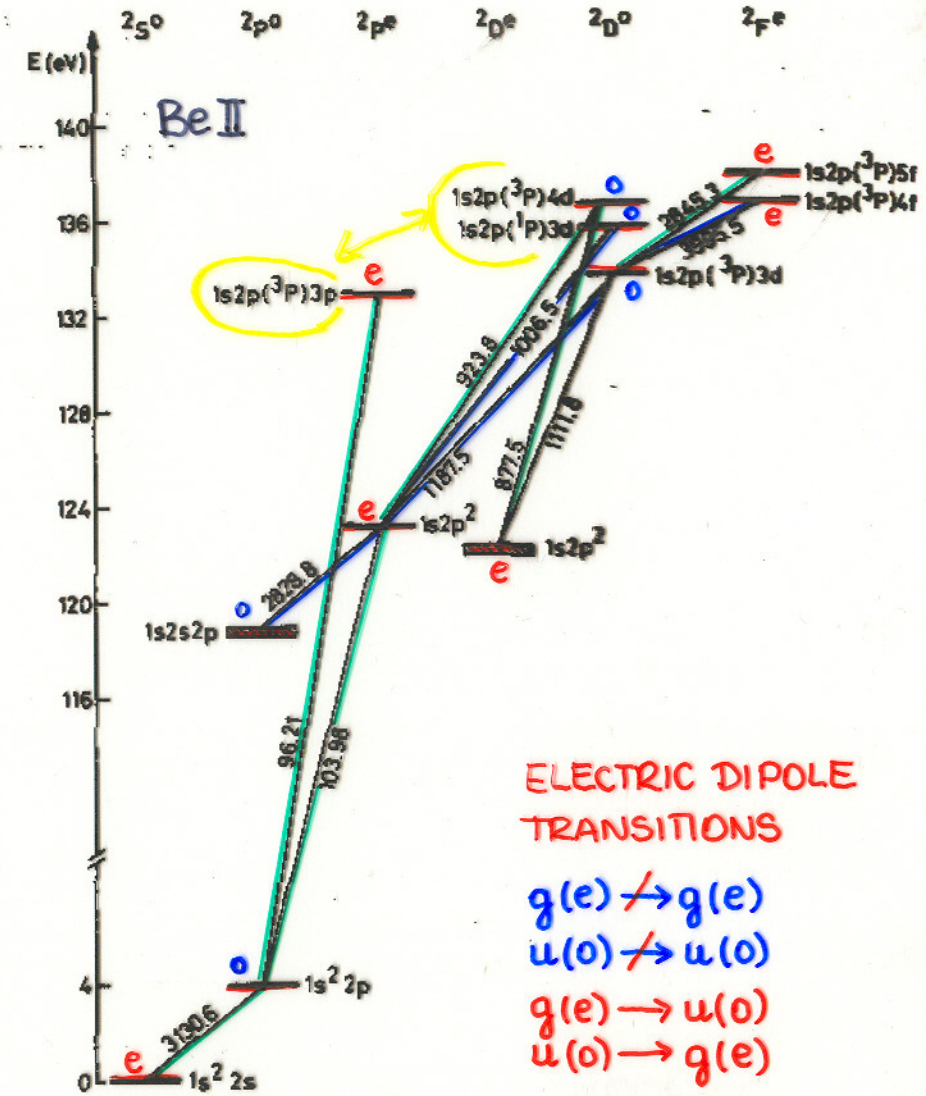


Fig. 2. Partial energy-level diagram for core-excited Be II ^2L with the observed transitions indicated.

PROBLEMS

1. SHOW THAT $\langle \Psi_a^r | O_1 | \Psi_b^s \rangle$, WHERE $O_1 \equiv$ ONE-PARTICLE OPERATOR,

FOR EXAMPLE: $O_1 \equiv h$

$$\begin{cases} = 0 & a \neq b, \; r \neq s \\ \langle r|h|s\rangle & a = b, \; r \neq s \\ -\langle b|h|a\rangle & a \neq b, \; r = s \\ \sum_c \{\langle c|h|c\rangle - \langle a|h|a\rangle + \langle r|h|r\rangle & a = b, \; r = s \end{cases}$$

2. IF $|K\rangle = |\chi_1, \chi_2, \chi_3\rangle$ (SLATER DETERMINANT)

SHOW THAT

$$\langle K|H|K\rangle = \langle 1|h|1\rangle + \langle 2|h|2\rangle + \langle 3|h|3\rangle + \langle 12||12\rangle + \langle 13||13\rangle + \langle 23||23\rangle$$

3. FIND THE ENERGY FOR THE DETERMINANT FUNCTION THAT DESCRIBES THE FOLLOWING ELECTRON CONFIGURATIONS