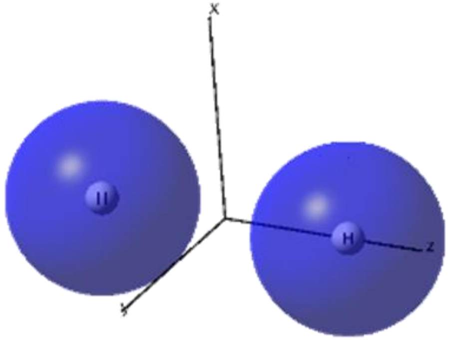
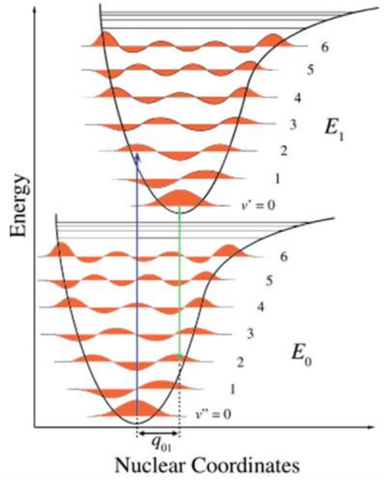
COLUMBUS
IN JOÃO PESSOA
November 07-09, 2019
João Pessoa - Paraíba

ONDE O SOL
NASCE PRIMEIRO!



DIATOMIC MOLECULES: POTENTIAL CURVES



Francisco B. C. Machado, Rene Felipe Keidel Spada
Instituto Tecnológico de Aeronáutica , SP, Brazil

Web page: http://www.univie.ac.at/columbus

Hamiltonian Operator

$$\hat{H}\psi = E\psi$$

Electron kinetic energy

Electron-Electron repulsion

$$\hat{H} = -\sum_{i=1}^{N}\frac{1}{2}\nabla_i^2 + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}} - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}}$$

Electron-nuclear attraction

$$-\sum_{A=1}^{M}\frac{1}{2}\nabla_A^2 + \sum_{A=1}^{M}\sum_{B>1}^{M}\frac{Z_A Z_B}{R_{AB}}$$

Nuclear kinetic energy

Nuclear-nuclear repulsion

Born-Oppenheimer Approximation

$$\psi(r,R)=\psi_{ele}(r;R)\phi_{nuc}(R)$$

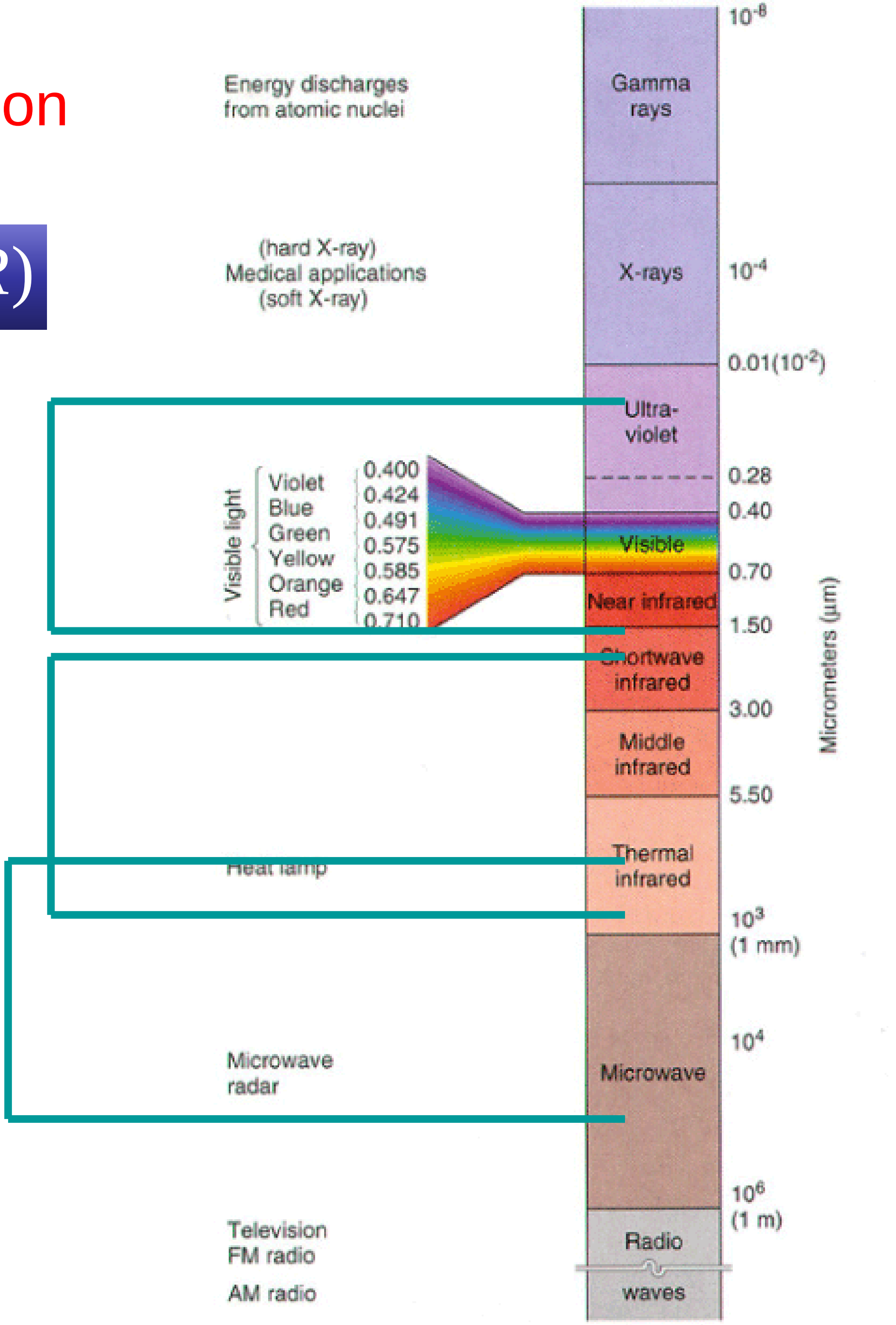
$$\psi_{ele}(r;R)$$

Eletronic Spectra

$$\phi_{nuc}(R)$$

Vibracional Spectra

Rotational Spectra



source: Christopherson (2000) *Geosystems*

I)

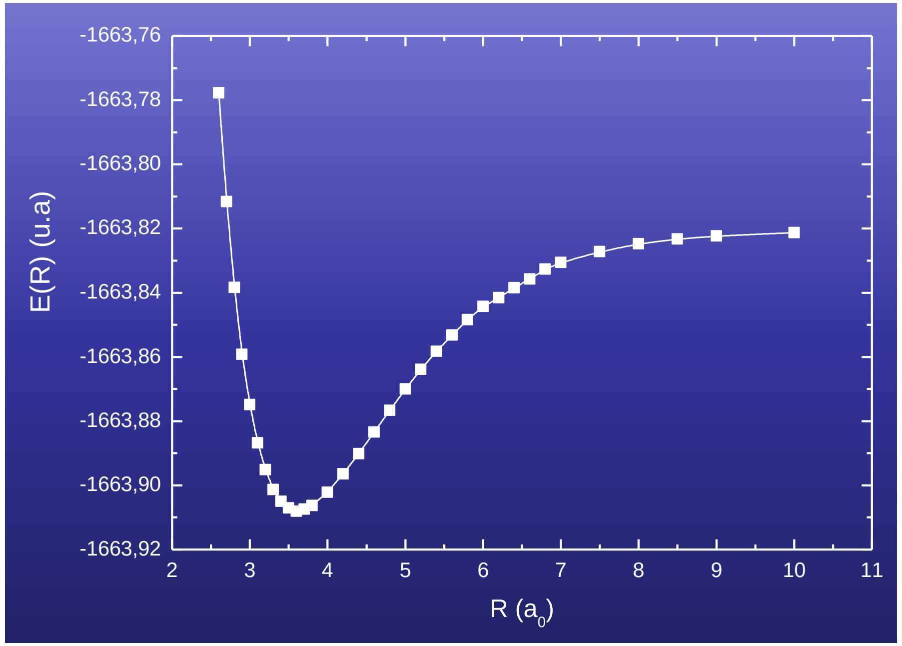
$$\hat{H}_{ele} = -\sum_{i=1}^{N}\frac{1}{2}\nabla_i^2 + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}} - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}}$$

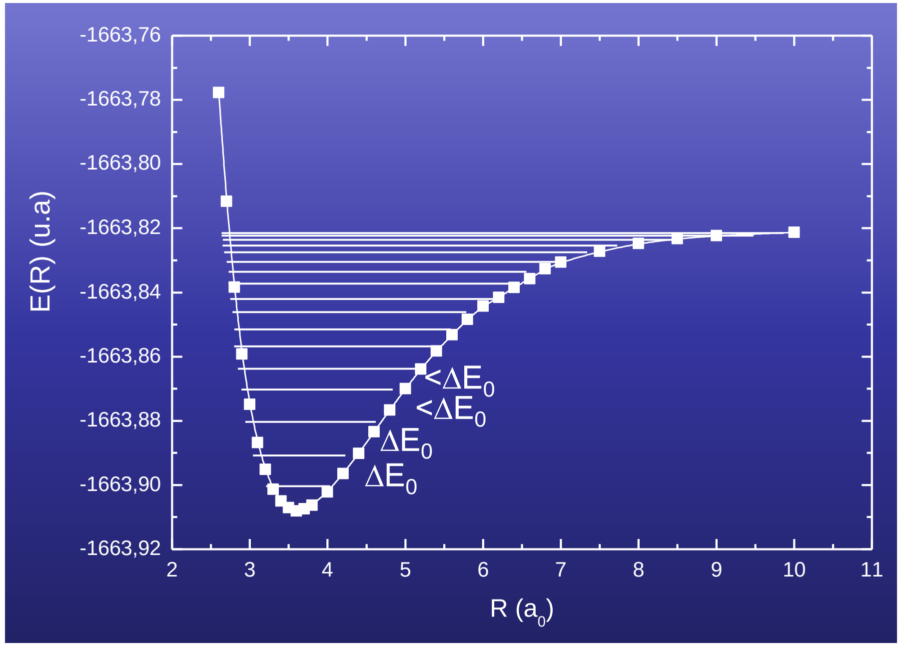
$$\hat{H}_{ele}\psi_{ele}(r;R) = E_{ele}(R)\psi_{ele}(r;R)$$

II)

$$\hat{H}_{nuc} = \left\langle -\sum_{i=1}^{N}\frac{1}{2}\nabla_i^2 + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}} - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} \right\rangle + -\sum_{A=1}^{M}\frac{1}{2}\nabla_A^2 + \sum_{A=1}^{M}\sum_{B>1}^{M}\frac{Z_A Z_B}{R_{AB}}$$

$$\hat{H}_{nuc}\phi_{nuc}(R) = E\phi_{nuc}(R)$$


E(R) (u.a)
-1663,76
-1663,78
-1663,80
-1663,82
-1663,84
-1663,86
-1663,88
-1663,90
-1663,92
2
3
4
5
6
7
8
9
10
11
R (a_0)

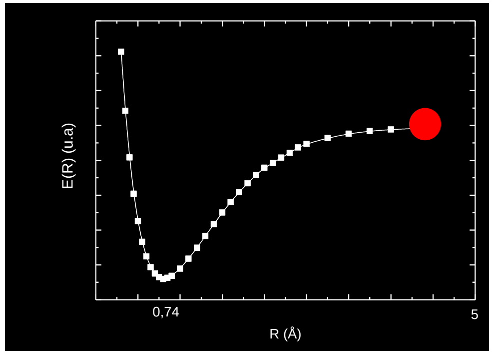

E(R) (u.a)
-1663,76
-1663,78
-1663,80
-1663,82
-1663,84
-1663,86
-1663,88
-1663,90
-1663,92
<ΔE_0
<ΔE_0
ΔE_0
ΔE_0
2
3
4
5
6
7
8
9
10
11
R (a_0)

Hydrogen Molecule (H_2):

$$R >> R_e$$

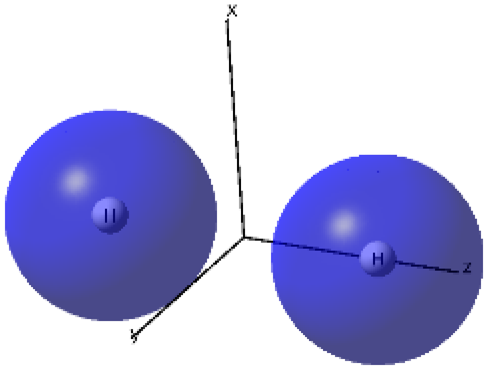
$$\psi(x_1, x_2) = \left| X_1 X_2 \right\rangle$$

$$X_j = C_1(1s') + C_2(1s'')$$



$$X_1 \cong 1(1s') + 0(1s'')$$

$$X_2 \cong 0(1s') + 1(1s'')$$



$$R \cong R_e$$

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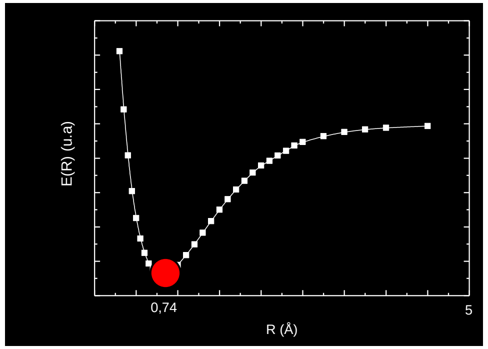
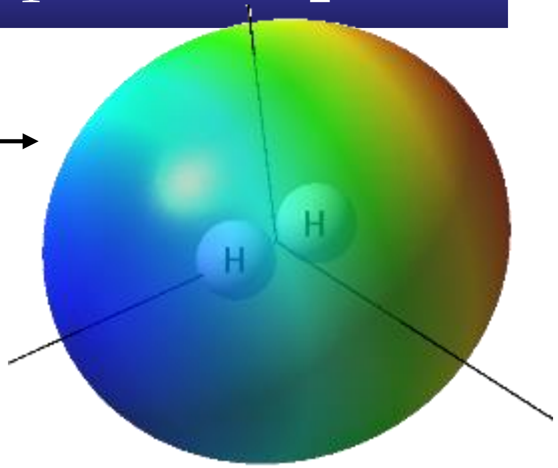


$$X_1 \cong \frac{1}{\sqrt{2}}\left[(1s') + (1s'')\right]$$

→

$$X_2 \cong \frac{1}{\sqrt{2}}\left[(1s') - (1s'')\right]$$



Hydrogen Molecule (H_2):

$$R >> R_e$$

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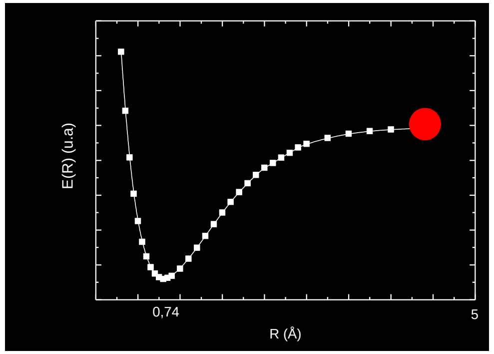
$$X_j = C_1(1s') + C_2(1s'')$$



$$X_1 \cong 1(1s') + 0(1s'')$$

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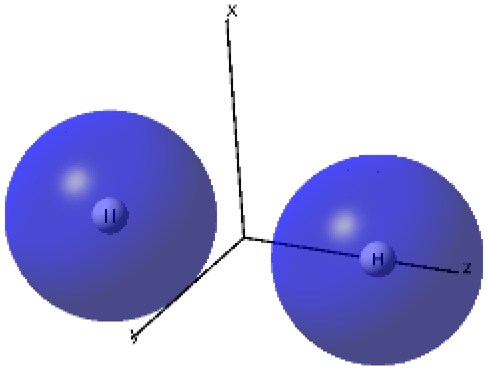
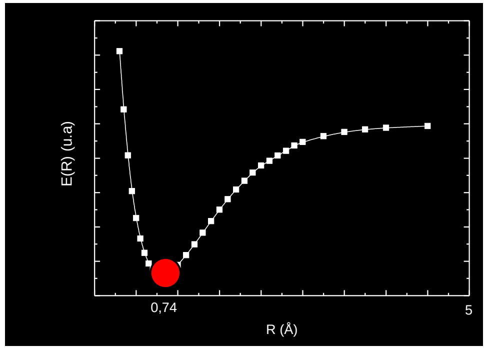


$$R \cong R_e$$

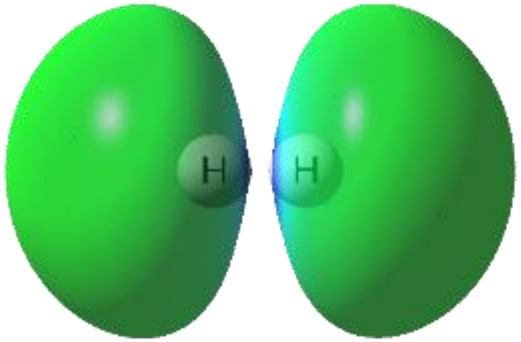
$$\psi(x_1, x_2) = \left| X_1 X_2 \right\rangle$$

$$X_j = C_1(1s') + C_2(1s'')$$



$$X_1 \cong \frac{1}{\sqrt{2}}\left[(1s') + (1s'')\right]$$

$$X_2 \cong \frac{1}{\sqrt{2}}\left[(1s') - (1s'')\right] \rightarrow$$

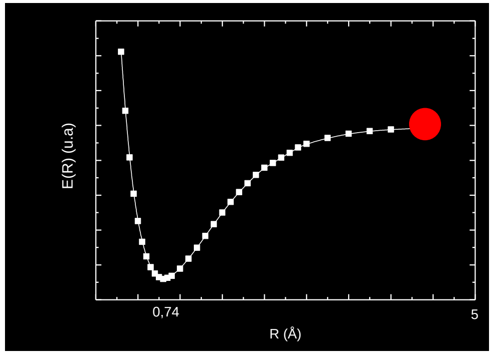


Hydrogen Molecule (H_2):

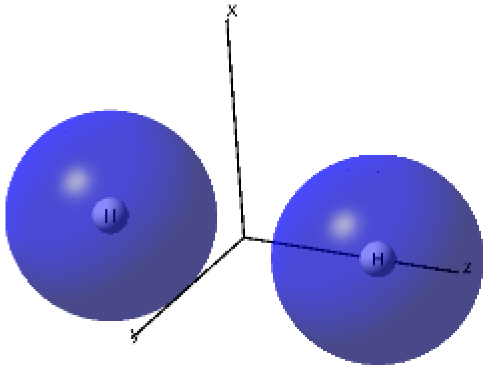
$$R >> R_e$$

$$\psi(x_1, x_2) = \left| X_1 X_2 \right\rangle$$

$$X_j = C_1(1s') + C_2(1s'')$$



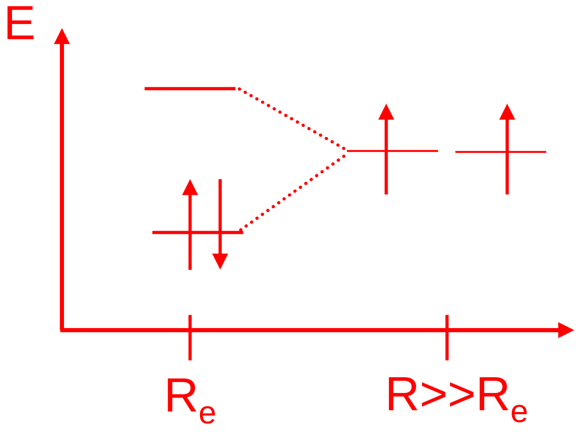
$$\begin{cases} X_1 \cong 1(1s') + 0(1s'') \\ X_2 \cong 0(1s') + 1(1s'') \end{cases}$$



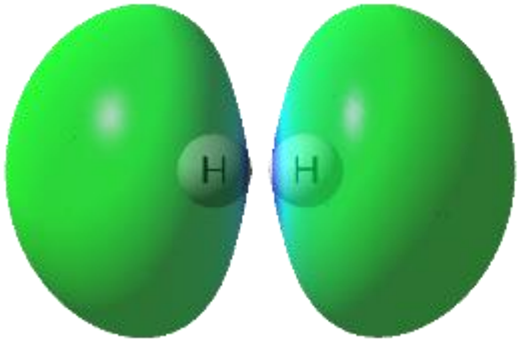
$$R \cong R_e$$

$$\psi(x_1, x_2) = \left| X_1 X_2 \right\rangle$$

$$X_j = C_1(1s') + C_2(1s'')$$



$$\begin{cases} X_1 \cong \dfrac{1}{\sqrt{2}}\left[(1s') + (1s'')\right] \\ X_2 \cong \dfrac{1}{\sqrt{2}}\left[(1s') - (1s'')\right] \rightarrow \end{cases}$$



Multireference Methods

- In Re Hartree-Fock ≈ 99% E_{exact}
- Erro ≈1% ≈ 1 eV ≈ 100 kJ/mol ≈ 25 kcal/mol
- Chemical bond ≈ 1 eV ≈ 100kJ/mol ≈ 25 kcal/mol

(energy difference)

Correlation energy

$$E_{corr} = E_{exact} - E_{HF}$$

H. Lischka, et al., *Chem. Rev.*, **118**, 7293 (2018)

Multireference Methods

- Separation of the whole calculation into two steps: (i) a reference configuration set describing the most relevant part (*quasi-degeneracies, nondynamic or static electron correlation*), using the multiconfiguration self consistent field (**MCSCF**) method and (ii) configuration interaction (CI) with all single and double excitations (*dynamic electron correlation*) – **MR-CISD**
- Size extensivity corrections: Davidson correction (+Q)

H. Lischka, et al., *Chem. Rev.*, **118**, 7293 (2018)

Multiconfigurational self-consistent field (MCSCF)

$$|\psi\rangle_{MCSCF} = \sum_{I} c_I |\psi_I\rangle$$

$$|\psi_I\rangle = |X_1 X_2 \ldots X_i X_b \ldots X_N\rangle$$

$$X_i = \sum_{\mu=1}^{K} C_{\mu i} \phi_\mu \qquad i = 1, 2, \ldots., K$$

H. Lischka, et al., *Chem. Rev.*, **118**, 7293 (2018)

Complete active space self-consistent field (CASSCF)

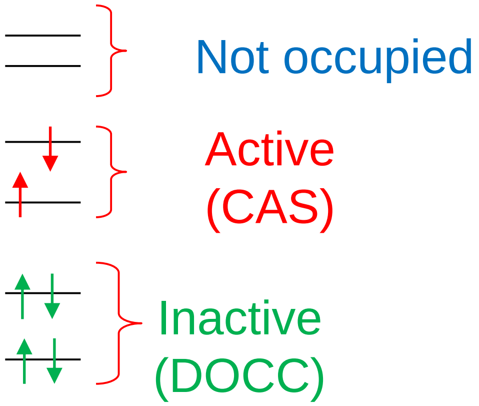
$$\left\{ \left| \psi_I \right\rangle \right\} = ?$$

Sometime, easy, dificult, impossible ...

Chemical information about the system

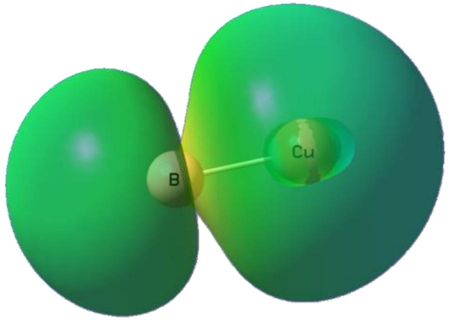
Necessary: MO occupation 0.1 – 1.9

Ideally: MO occupation 0.02 - 1.98

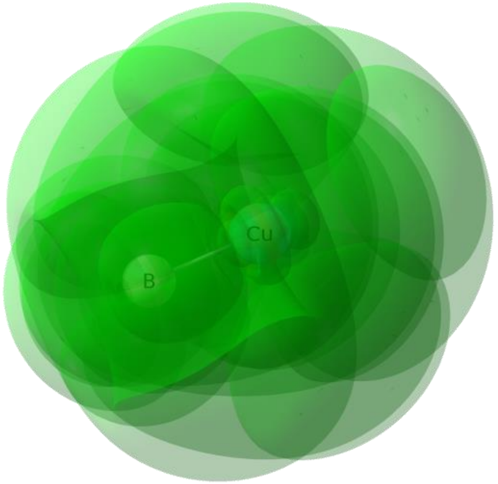


H. Lischka, et al., *Chem. Rev.*, **118**, 7293 (2018)

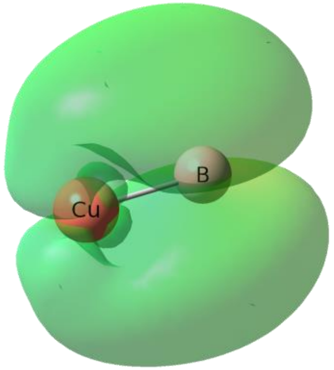
Complete active space self-consistent field (CASSCF)



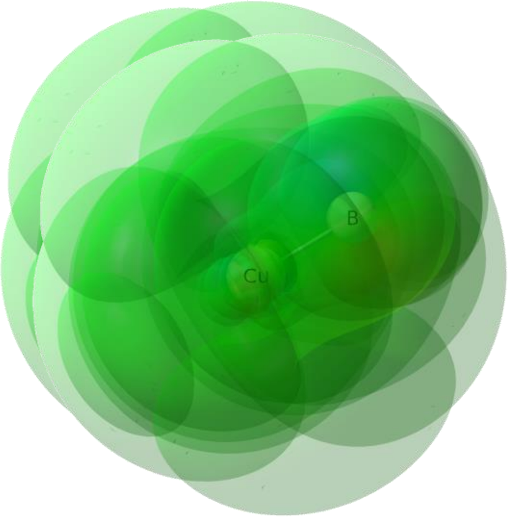
CuB ($^1\Sigma^+$) – HOMO ($9\sigma^2$)



CAS ($7\sigma 8\sigma 9\sigma 10\sigma 11\sigma 3\pi 4\pi 5\pi 1\delta$)



CuB$^-$ $^2\Pi$ – HOMO ($4\pi^1$)



H. Lischka, et al., *Chem. Rev.*, **118**, 7293 (2018)

Configuration Interaction, CI

Virtual Orbitals $$\left\{ X_{N+1} X_{N+2} \cdots X_r X_s \cdots X_k \right\}$$

Occupeid Orbitals $$\left\{ X_1 X_2 \cdots X_a X_b \cdots X_N \right\}$$

$$\left| \psi_0 \right\rangle = \left| X_1 X_2 \cdots X_a X_b \cdots X_N \right\rangle$$

$$\left| \psi_a^r \right\rangle = \left| X_1 X_2 \cdots X_r X_b \cdots X_N \right\rangle$$

$$\left| \psi_{ab}^{rs} \right\rangle = \left| X_1 X_2 \cdots X_r X_s \cdots X_N \right\rangle$$

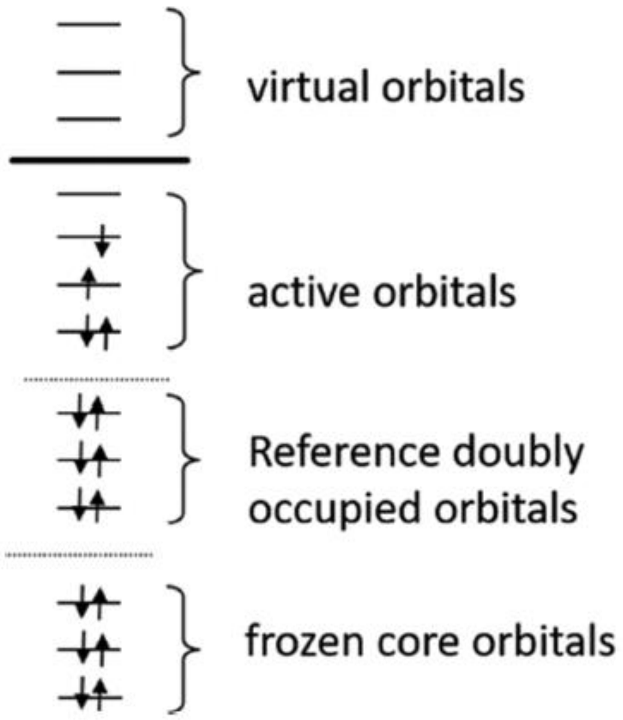
$$X_i = \sum_{\mu=1}^{K} C_{\mu i} \phi_\mu \qquad i = 1, 2, \ldots, K$$

H. Lischka, et al., *Chem. Rev.*, **118**, 7293 (2018)

MRSDCI

$$\left|\Phi_0\right\rangle_{MRSDCI} = \left\{\left|\psi_0\right\rangle\right\} + \sum_{ar} c_a^r \left\{\left|\psi_a^r\right\rangle\right\} + \sum_{\substack{a<b \\ r<s}} c_{ab}^{rs} \left\{\left|\psi_{ab}^{rs}\right\rangle\right\}$$

$$\left\{\left|\psi_0\right\rangle\right\} = ?$$



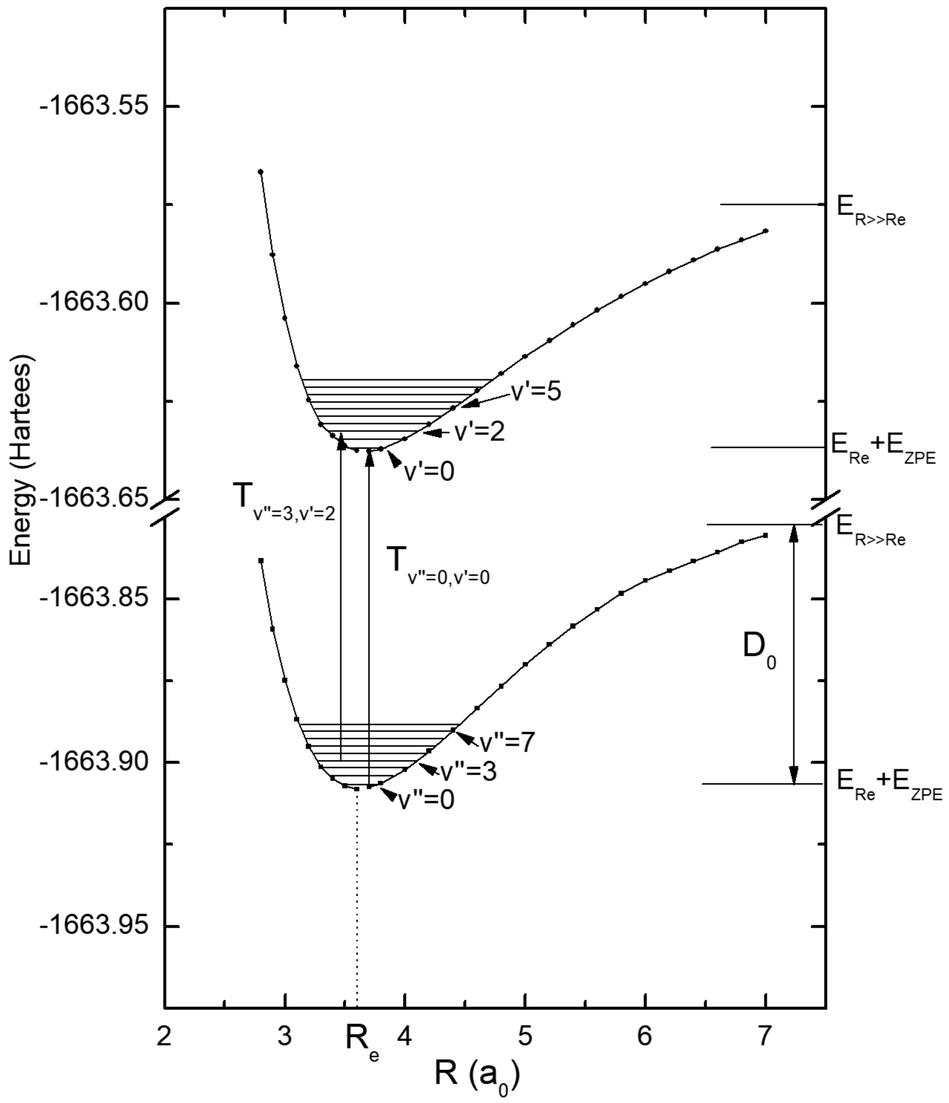
Davidson correction (+Q)

$$\Delta E_Q = (1 - c_0^2)(E_{CISD} - E_{HF})$$

S. R. Langhoff, E. R. Davidson, *Inter. J. Quant.Chem.*, **8**, 61, (1974)

H. Lischka, et al., *Chem. Rev.*, **118**, 7293 (2018)

- Methodology
- CASSCF (active space = valence)
- MRCI
- Basis set
- Nuclear Equation – DSITA Program
- Transition Probabilities
- $A_{\nu'\nu''} = |\langle \nu'|\mu_{TM}(R)|\nu''\rangle|^2 \nu^3_{\nu'\nu''} \frac{(2-\delta_{0,\Lambda'+\Lambda''})}{(2-\delta_{0,\Lambda'})}$
- Radiative Lifetimes **($1/A_{\nu'\nu''}$)**
- photoionization transition
- $I(\nu',\nu'') \sim |M_e|^2 |\langle \nu''|\nu'\rangle|^2 = |M_e|^2 Q_{\nu''\nu'}$



Diatomic Molecules – State of art

- Natural candidates to test methodologies.
- Ideally, full CI : Very expensive.
- Dissociation energies, electronic and rovibrational

  Spectroscopy, excited states: require multireference methodologies.
- Main group elements: CASSCF/MRCI
- More challenge: systems with, at least, one transition metal atom

H. Lischka, et al., *Chem. Rev.*, **118**, 7293 (2018)

MRCI: Performance of the Contract Methods

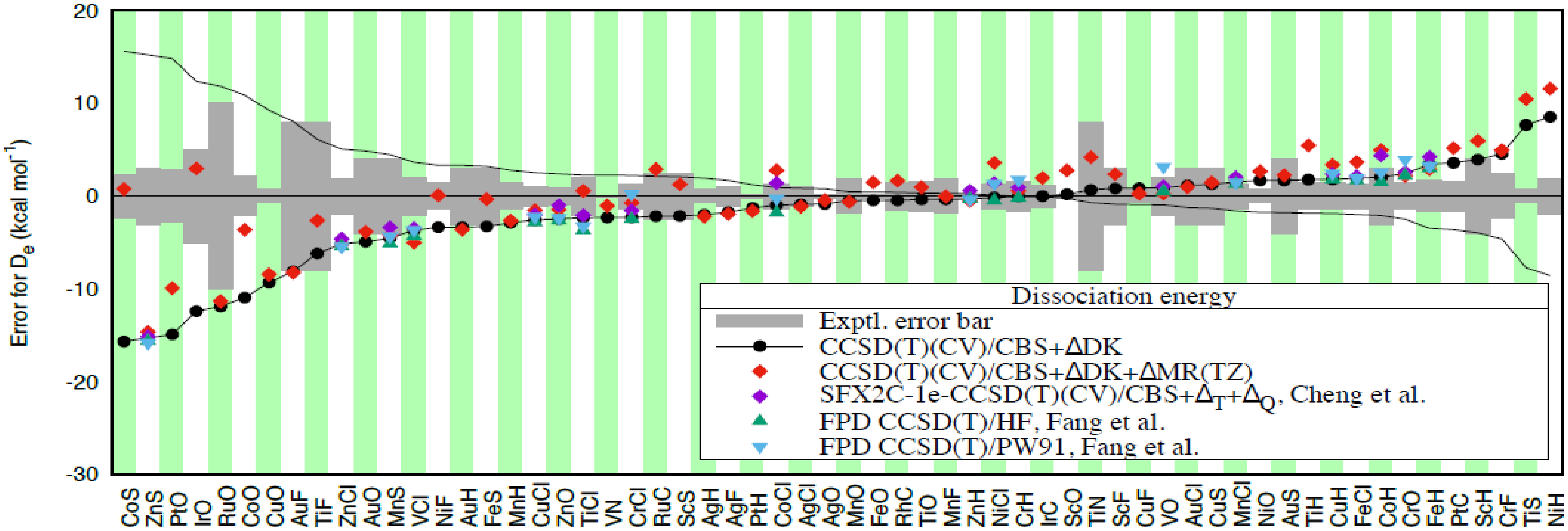
Molecule	State	PC-MRCI	FIC-MRCI	SC-MRCI	SC-MRCI(L.Ext)	ΔER
CH	$^2\Pi$	0.8	1.2	3.9	9.1	0.3
	$^2\Delta$		0.8	4.3	9.0	0.3
	$^2\Sigma^-$		1.6	4.3	9.0	0.6
CN	$^2\Sigma^+$		3.7	9.3	23.1	0.6
	$^2\Pi$		4.1	9.5	24.4	0.9
CO	$^1\Sigma^+$	3.3	4.5	11.3	27.5	1.5
	$^1\Pi$		6.1	15.9	33.4	1.7
	$^1\Sigma^-$		5.5	12.9	30.5	1.0
	$^1\Delta$		5.0	12.9	30.4	0.9
CO^+	$^2\Sigma^+$	2.4	3.1	9.0	19.3	0.9
	$^2\Pi$		4.4	10.6	22.0	1.8
	$2\text{-}^2\Sigma^+$		4.7	11.9	22.8	2.1
N_2	$^1\Sigma^+$	3.4	4.1	9.5	25.6	0.8
	$^1\Pi$		5.6	13.8	30.8	0.9
	$^1\Sigma^-$		6.1	12.7	30.4	1.0
O_2	$^1\Delta$	5.1	6.3	11.8	37.5	1.5
	$^1\Sigma^+$		5.7	11.2	37.5	1.2
	$^3\Sigma^+$	5.7	7.3	13.9	38.0	2.1
OH	$^2\Pi$	1.6	2.0	5.6	18.3	0.4
	$^2\Sigma^+$		2.4	5.8	18.6	0.9

in [mEh])

(a) the reference relaxation computed with uc-MRCI (ΔER) plays a minor role;
(b) FIC-MRCI misses 2%−3% of the correlation energy;
(c) The error ranges are substantially larger for SC-MRCI with values about 4%−6%;
(d) the orbital noninvariance calculated comparing SC-MRCI and SC-MRCI with localized virtual orbitals (SC -MRCI[LExt]) does not affect the excitation energies due to error cancellation;
(e) the excitation energies are in excellent agreement with the uc-MRCI results

H. Lischka, et al., *Chem. Rev.*, **118**, 7293 (2018)
K. Sivalingam, et al., J. Chem. Phys. **145**, 054104 (2016).

Deviations in the calculated dissociation energy from the exp. values for the 60 transition metal (TM) diatomic molecules

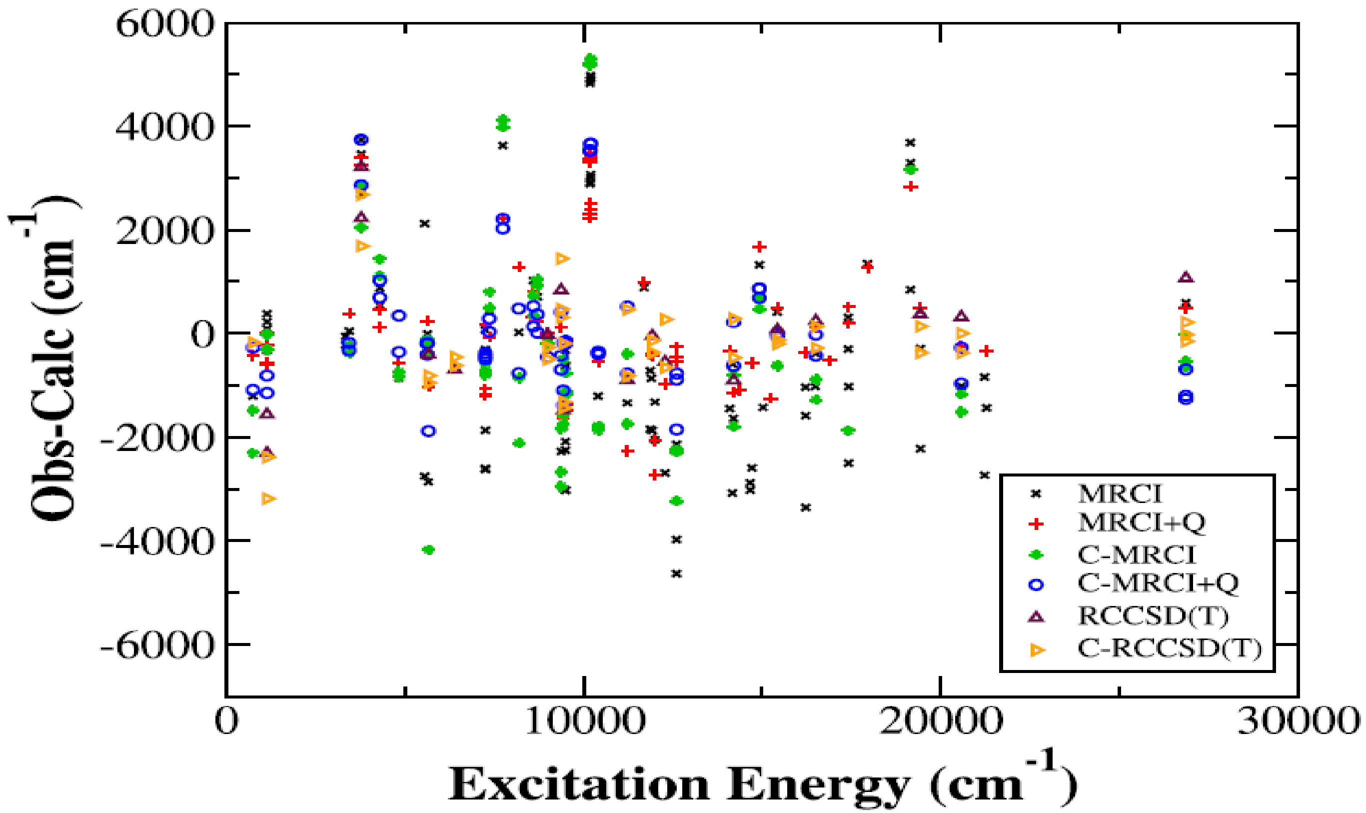


Mean absolute deviation (MAD) of 3.3 kcal mol^{-1}. Very high. Complexity to describe the bond-breaking of TM. For some cases it is 15 kcal mol^{-1}.

Suggestion: most of the experimentally derived values require careful revision.

H. Lischka, et al., *Chem. Rev.*, **118**, 7293 (2018)
Y. A. Aoto, et al., *J. Chem. Theory Comput.* **13**, 5291 (2017)

Electronic excitation energy calculations for diatomic transition metal oxides and compared with available experimental data



Erros: Better accurate is around 100 cm^{-1}. Most exceeds 1000 cm^{-1}, especially for the higher lying states

H. Lischka, et al., *Chem. Rev.*, **118**, 7293 (2018)
J. Tennyson, et al., *J. Phys. B At. Mol. Opt. Phys.*, **49**, 102001 (2016)

Characterization: Potential Energy Curves - Strategy

Previous Information?

- Ground State Configuration?
- Excited State Configuartion?
- Molecular Orbital Diagram?
- Experimental Assignment?
- Assintotic Limit – Atomic Level – in general available

Wigner-Witmer Rules

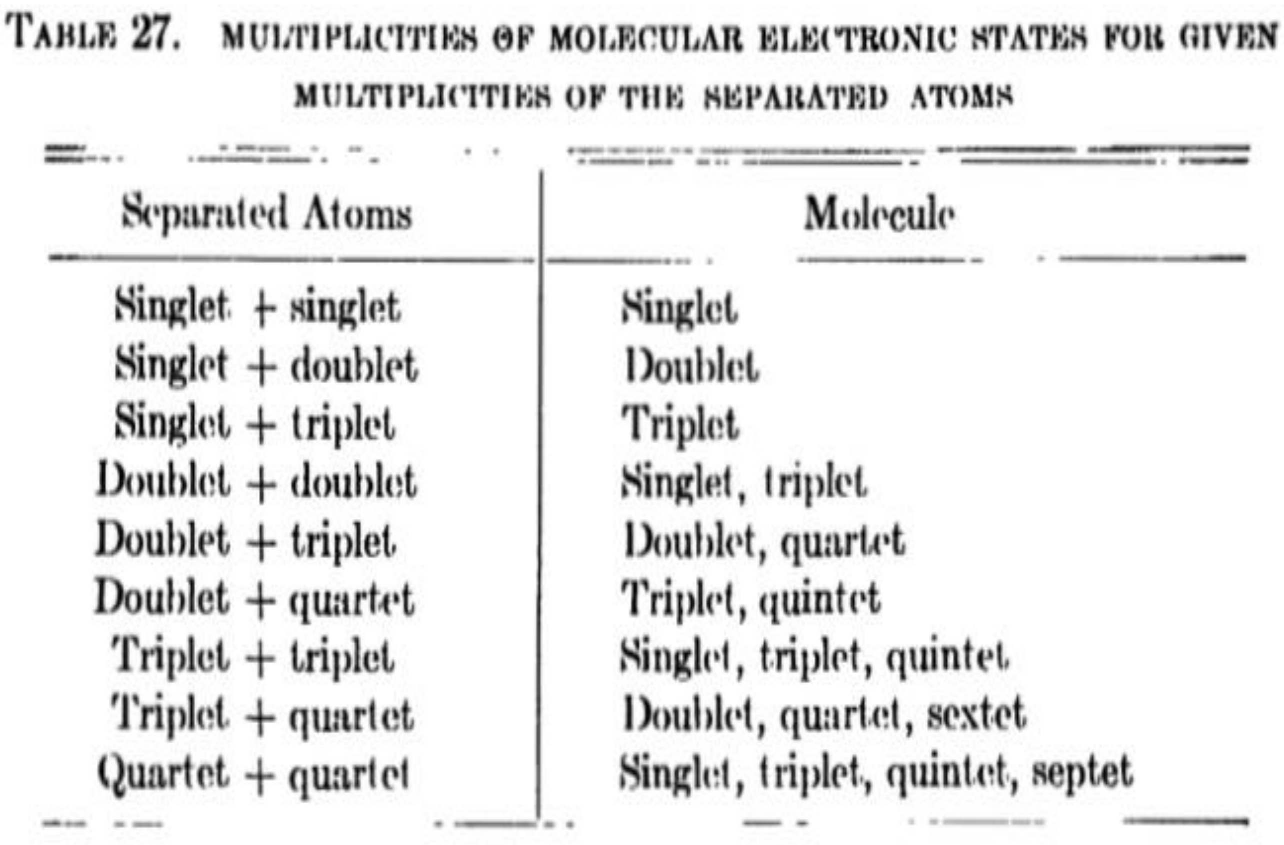


TABLE 27. MULTIPLICITIES OF MOLECULAR ELECTRONIC STATES FOR GIVEN MULTIPLICITIES OF THE SEPARATED ATOMS

Separated Atoms	Molecule
Singlet + singlet	Singlet
Singlet + doublet	Doublet
Singlet + triplet	Triplet
Doublet + doublet	Singlet, triplet
Doublet + triplet	Doublet, quartet
Doublet + quartet	Triplet, quintet
Triplet + triplet	Singlet, triplet, quintet
Triplet + quartet	Doublet, quartet, sextet
Quartet + quartet	Singlet, triplet, quintet, septet

G. Herzberg, Molecular Spectra and Molecular Structure. Vol. 1, van Nostrand Reinhold, New York, 1950.

Wigner-Witmer Rules

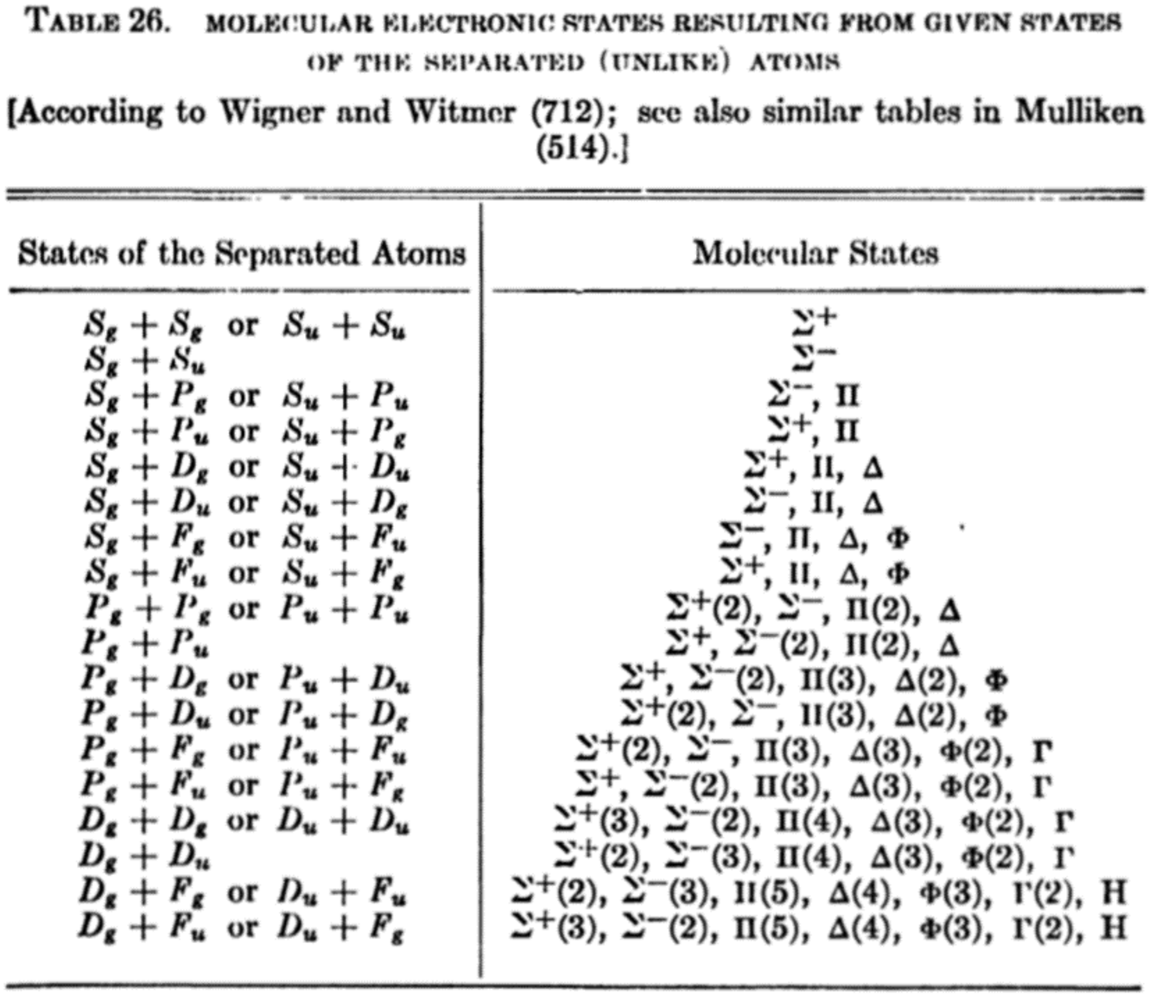


Table 26. MOLECULAR ELECTRONIC STATES RESULTING FROM GIVEN STATES OF THE SEPARATED (UNLIKE) ATOMS

[According to Wigner and Witmer (712); see also similar tables in Mulliken (514).]

States of the Separated Atoms	Molecular States
$S_g + S_g$ or $S_u + S_u$	Σ^+
$S_g + S_u$	Σ^-
$S_g + P_g$ or $S_u + P_u$	Σ^-, Π
$S_g + P_u$ or $S_u + P_g$	Σ^+, Π
$S_g + D_g$ or $S_u + D_u$	Σ^+, Π, Δ
$S_g + D_u$ or $S_u + D_g$	Σ^-, Π, Δ
$S_g + F_g$ or $S_u + F_u$	Σ^-, Π, Δ, Φ
$S_g + F_u$ or $S_u + F_g$	Σ^+, Π, Δ, Φ
$P_g + P_g$ or $P_u + P_u$	$\Sigma^+(2)$, Σ^-, $\Pi(2)$, Δ
$P_g + P_u$	Σ^+, $\Sigma^-(2)$, $\Pi(2)$, Δ
$P_g + D_g$ or $P_u + D_u$	Σ^+, $\Sigma^-(2)$, $\Pi(3)$, $\Delta(2)$, Φ
$P_g + D_u$ or $P_u + D_g$	$\Sigma^+(2)$, Σ^-, $\Pi(3)$, $\Delta(2)$, Φ
$P_g + F_g$ or $P_u + F_u$	$\Sigma^+(2)$, Σ^-, $\Pi(3)$, $\Delta(3)$, $\Phi(2)$, Γ
$P_g + F_u$ or $P_u + F_g$	Σ^+, $\Sigma^-(2)$, $\Pi(3)$, $\Delta(3)$, $\Phi(2)$, Γ
$D_g + D_g$ or $D_u + D_u$	$\Sigma^+(3)$, $\Sigma^-(2)$, $\Pi(4)$, $\Delta(3)$, $\Phi(2)$, Γ
$D_g + D_u$	$\Sigma^+(2)$, $\Sigma^-(3)$, $\Pi(4)$, $\Delta(3)$, $\Phi(2)$, Γ
$D_g + F_g$ or $D_u + F_u$	$\Sigma^+(2)$, $\Sigma^-(3)$, $\Pi(5)$, $\Delta(4)$, $\Phi(3)$, $\Gamma(2)$, H
$D_g + F_u$ or $D_u + F_g$	$\Sigma^+(3)$, $\Sigma^-(2)$, $\Pi(5)$, $\Delta(4)$, $\Phi(3)$, $\Gamma(2)$, H

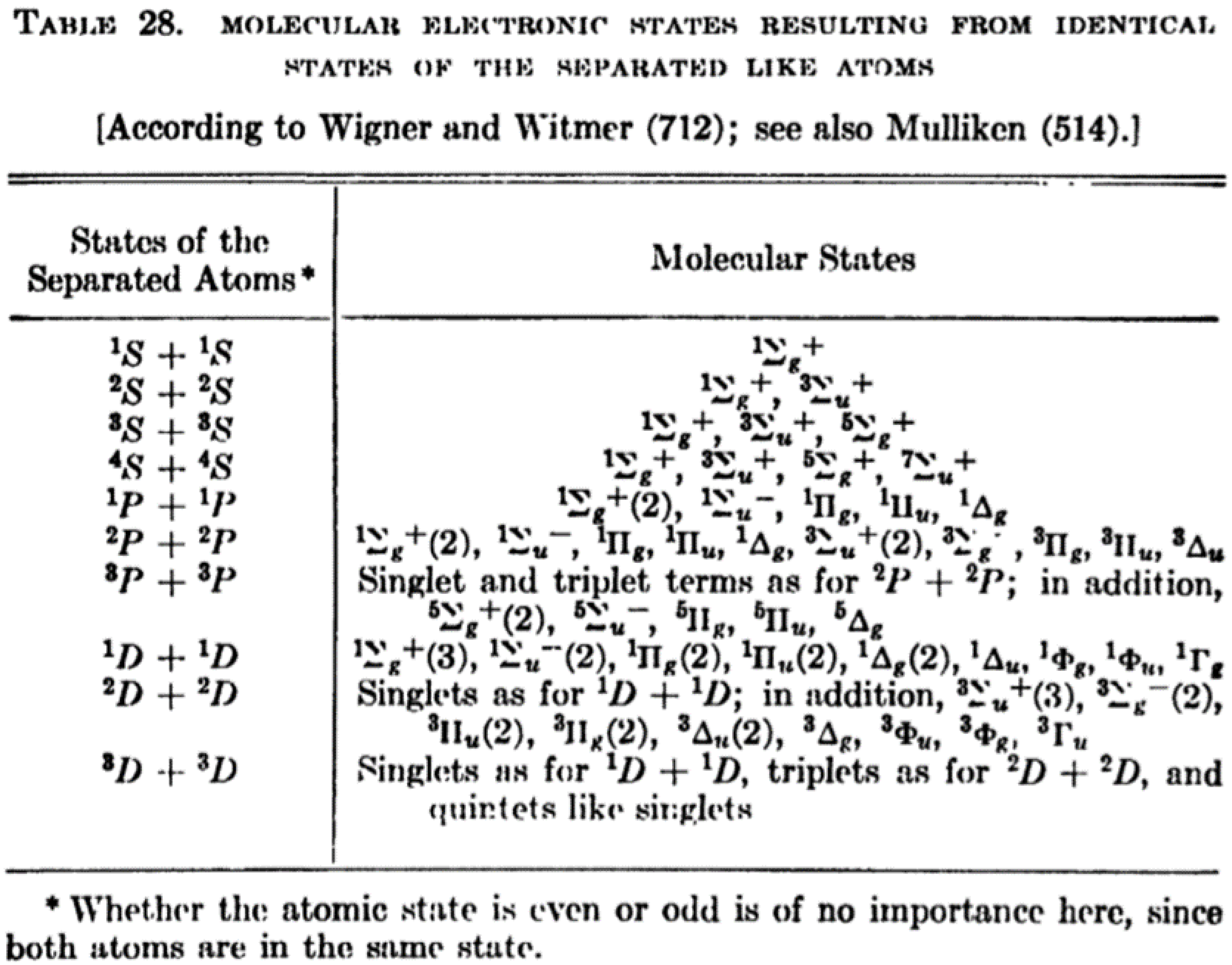


Table 28. MOLECULAR ELECTRONIC STATES RESULTING FROM IDENTICAL STATES OF THE SEPARATED LIKE ATOMS

[According to Wigner and Witmer (712); see also Mulliken (514).]

States of the Separated Atoms*	Molecular States
$^1S + {}^1S$	$^1\Sigma_g^+$
$^2S + {}^2S$	$^1\Sigma_g^+$, $^3\Sigma_u^+$
$^3S + {}^3S$	$^1\Sigma_g^+$, $^3\Sigma_u^+$, $^5\Sigma_g^+$
$^4S + {}^4S$	$^1\Sigma_g^+$, $^3\Sigma_u^+$, $^5\Sigma_g^+$, $^7\Sigma_u^+$
$^1P + {}^1P$	$^1\Sigma_g^+(2)$, $^1\Sigma_u^-$, $^1\Pi_g$, $^1\Pi_u$, $^1\Delta_g$
$^2P + {}^2P$	$^1\Sigma_g^+(2)$, $^1\Sigma_u^-$, $^1\Pi_g$, $^1\Pi_u$, $^1\Delta_g$, $^3\Sigma_u^+(2)$, $^3\Sigma_g^-$, $^3\Pi_g$, $^3\Pi_u$, $^3\Delta_u$
$^3P + {}^3P$	Singlet and triplet terms as for $^2P + {}^2P$; in addition, $^5\Sigma_g^+(2)$, $^5\Sigma_u^-$, $^5\Pi_g$, $^5\Pi_u$, $^5\Delta_g$
$^1D + {}^1D$	$^1\Sigma_g^+(3)$, $^1\Sigma_u^-(2)$, $^1\Pi_g(2)$, $^1\Pi_u(2)$, $^1\Delta_g(2)$, $^1\Delta_u$, $^1\Phi_g$, $^1\Phi_u$, $^1\Gamma_g$
$^2D + {}^2D$	Singlets as for $^1D + {}^1D$; in addition, $^3\Sigma_u^+(3)$, $^3\Sigma_g^-(2)$, $^3\Pi_u(2)$, $^3\Pi_g(2)$, $^3\Delta_u(2)$, $^3\Delta_g$, $^3\Phi_u$, $^3\Phi_g$, $^3\Gamma_u$
$^3D + {}^3D$	Singlets as for $^1D + {}^1D$, triplets as for $^2D + {}^2D$, and quintets like singlets

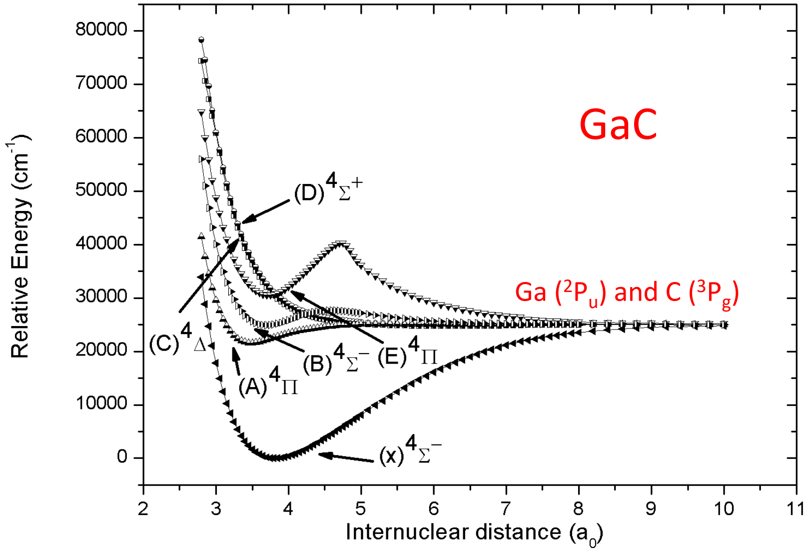
* Whether the atomic state is even or odd is of no importance here, since both atoms are in the same state.

G. Herzberg, Molecular Spectra and Molecular Structure. Vol. 1, van Nostrand Reinhold, New York, 1950.

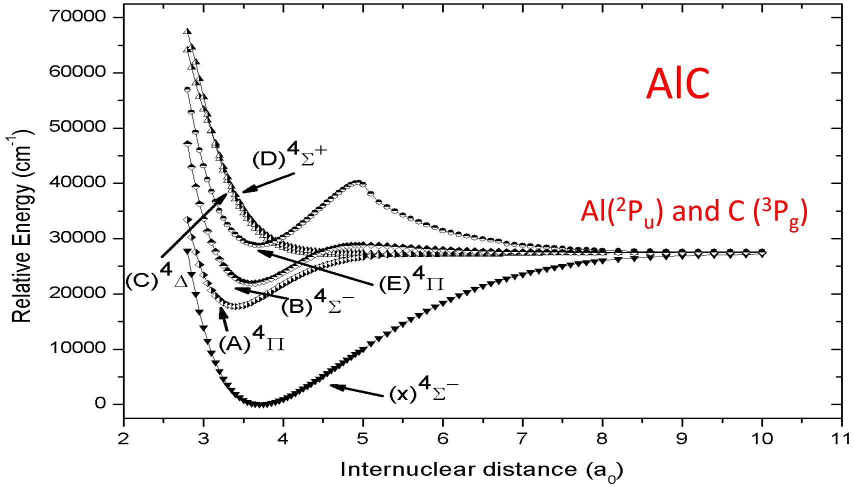
Studied Molecules: AlC, GaC

Electronic states correlated to the first dissociation channels of AlC and GaC molecules.

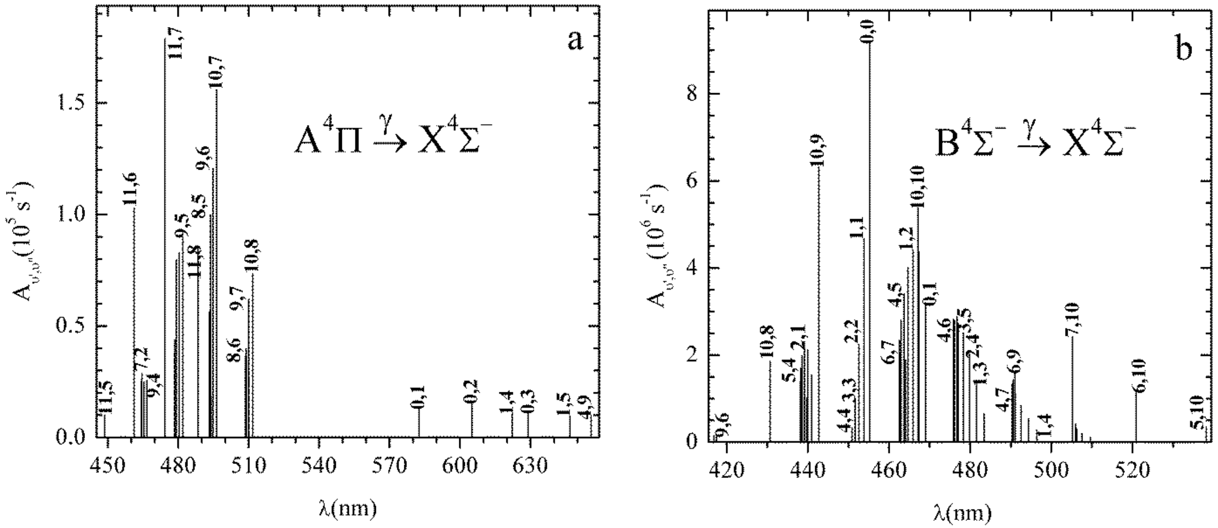
	Electronic states	Spin multiplicity	Dissociation channels	Energy (cm^{-1})
1st	Σ^+, $\Pi(2)$, Δ, $\Sigma^-(2)$	doublet, quartet	Al / Ga (^2P_u) + C (^3P_g)	0
2nd	Σ^+, $\Pi(3)$, $\Delta(2)$, $\Sigma^-(2)$, Φ	doublet	Al / Ga (^2P_u) + C (^1D_u)	10192
3rd	Σ^-, Π	doublet	Al / Ga (^2P_u) + C (^1S_u)	21648
4th	Σ^-, Π	doublet, quartet	Al / Ga (^2S_g) + C (^3P_g)	25347/24788



Active Space: Valence (7e,8o) + 4s (Al) +2σ + 1π



AlC: Emission coefficient as function of the wavelength



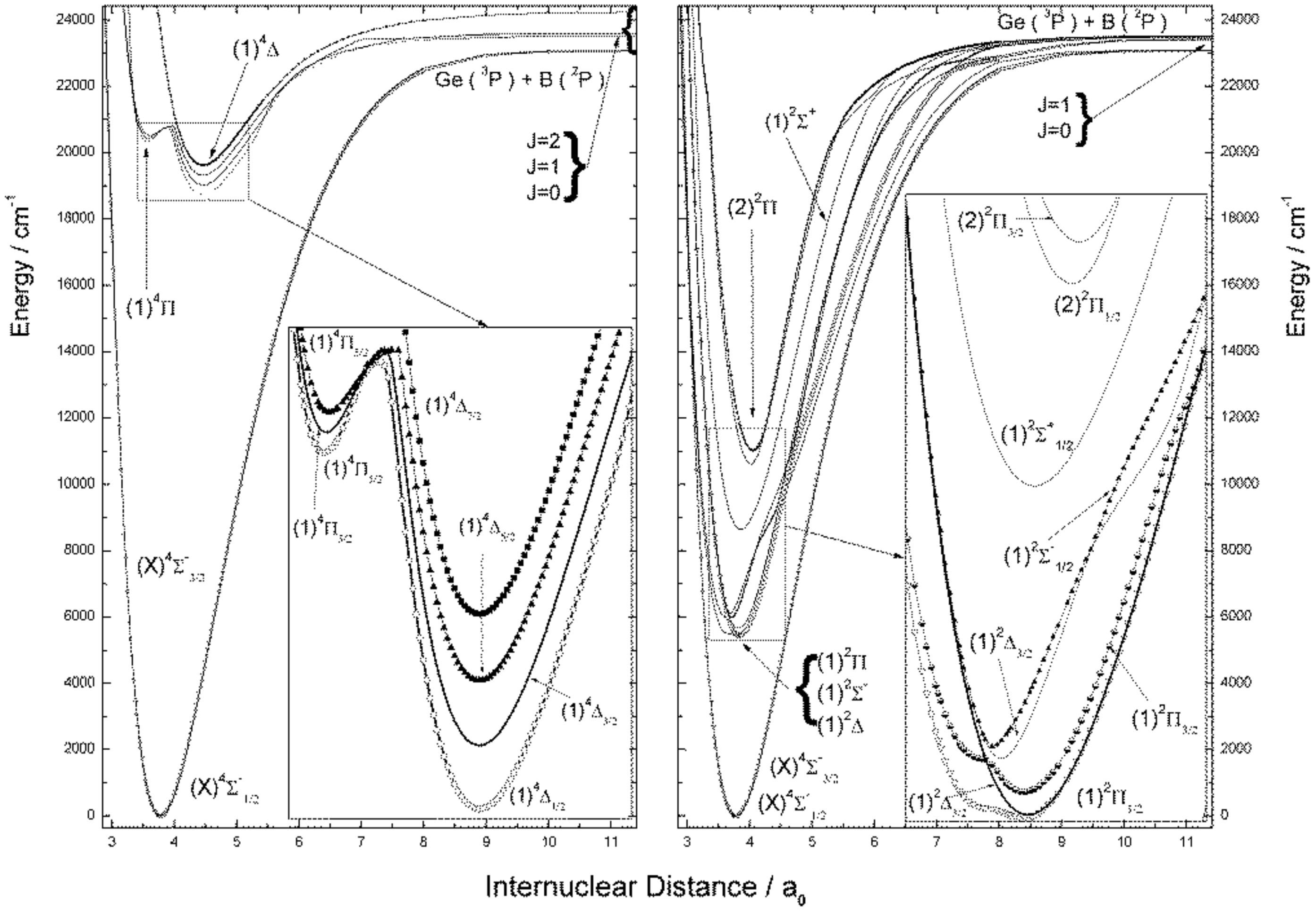
Avoided crossing: Π states

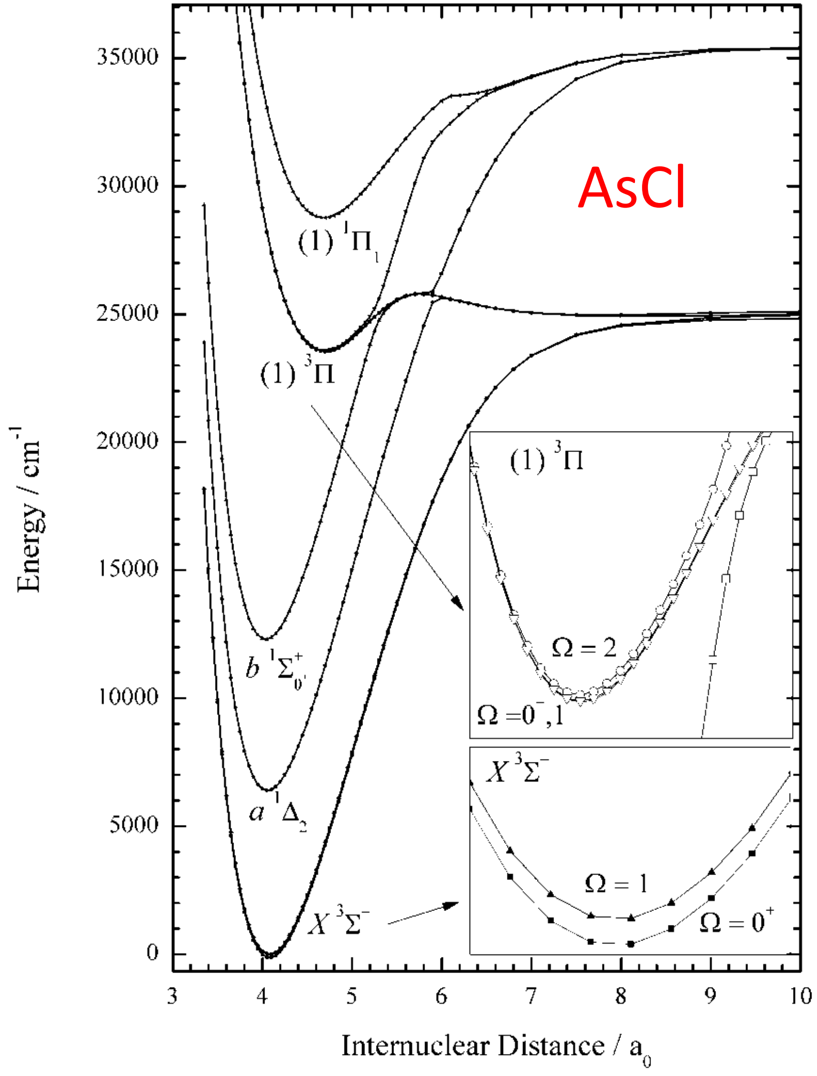
Al(^2P_u) → Al(^2S_g)

Chem . Phys. Lett., **687**, 171 (2017)

Studied Molecules: AsCl, GeB

GeB

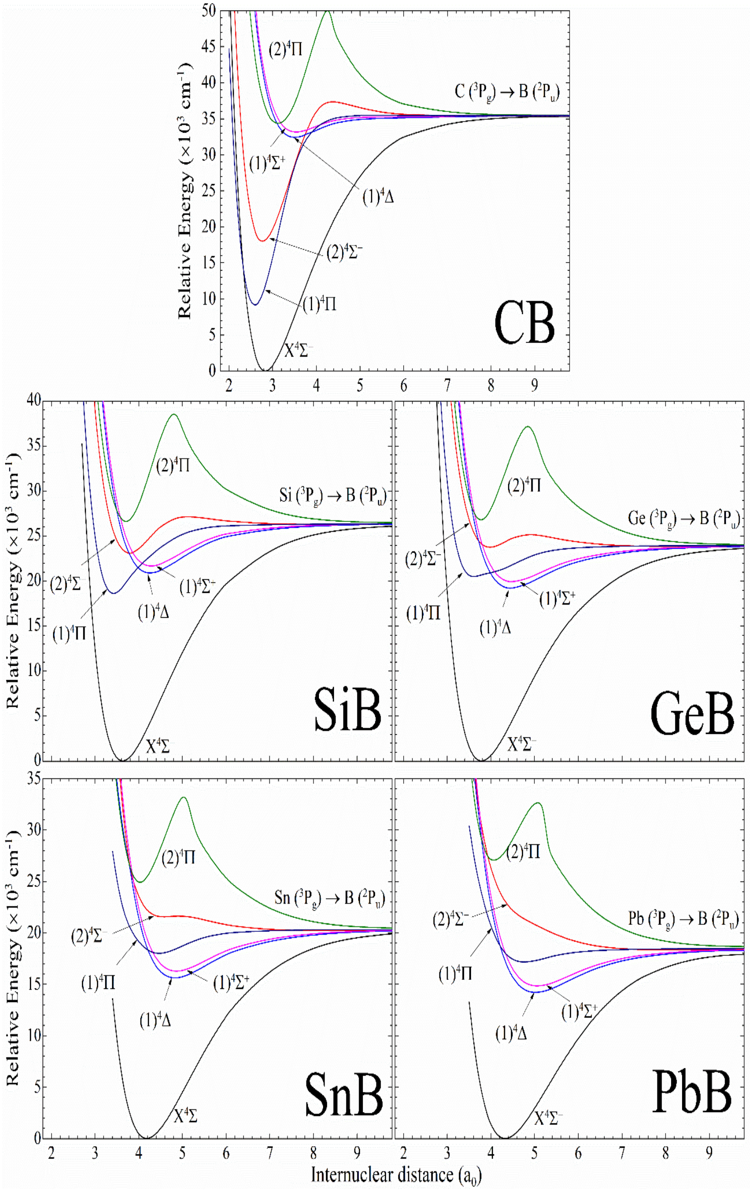


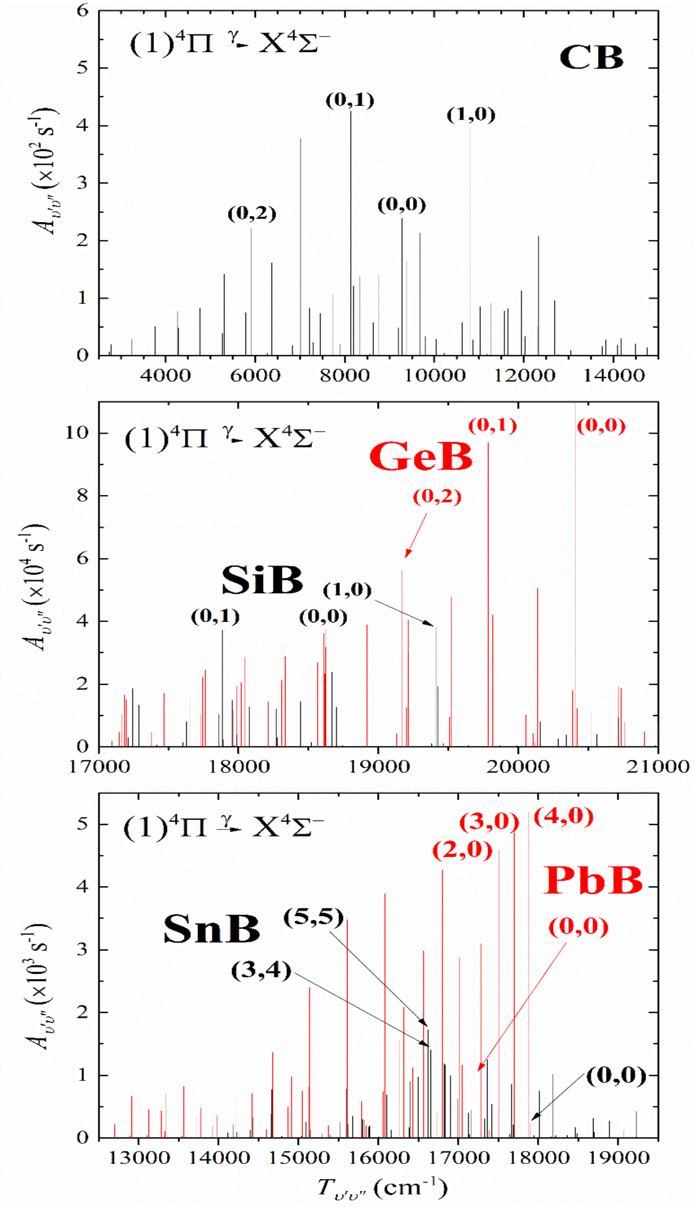


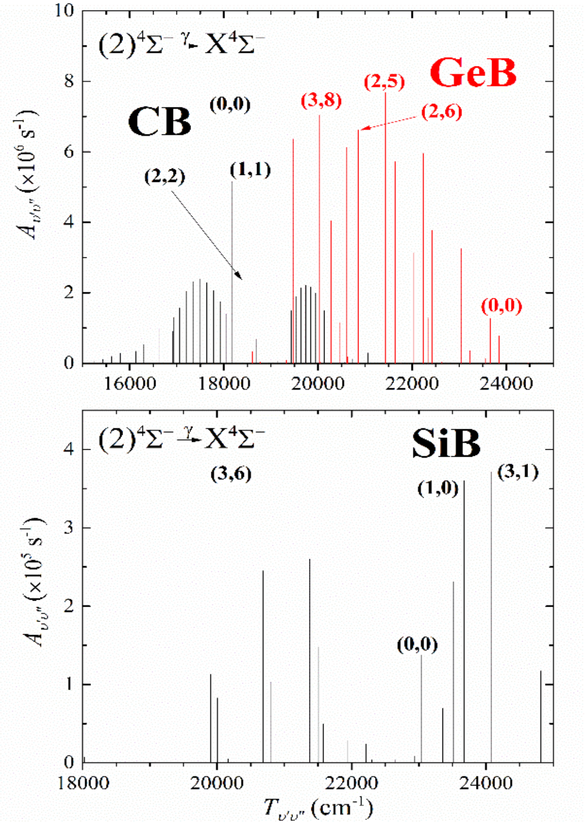
Chem . Phys. Lett., **601**, 26 (2014)

Chem . Phys. Lett., **634**, 66 (2015)

Studied Molecules: XB (X = C, Si, Ge, Sn, Pb)







J. Quant. Spectrosc. Radiat. Transfer, **209**, 156 (2018)

Studied Molecules: CuB, CuAl, CuB^+, $CuAl^+$

[core] {active}

- **Outer valence (OV)**

Cu $[1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}]$ $\{4s^1 4p^0\}$

X $[1s^2]$ $\{2s^2 2p^{N_x}\}$

OV ~100 CFS

- **Inner valence (IV)**

Cu $[1s^2 2s^2 2p^6 3s^2 3p^6]$ $\{3d^{10} 4s^1\}$

X $[1s^2]$ $\{2s^2 2p^{N_x}\}$

IV ~800 CFS

- **“Full” valence (FV)**

Cu $[1s^2 2s^2 2p^6 3s^2 3p^6]$ $\{3d^{10} 4s^1 4p^0\}$

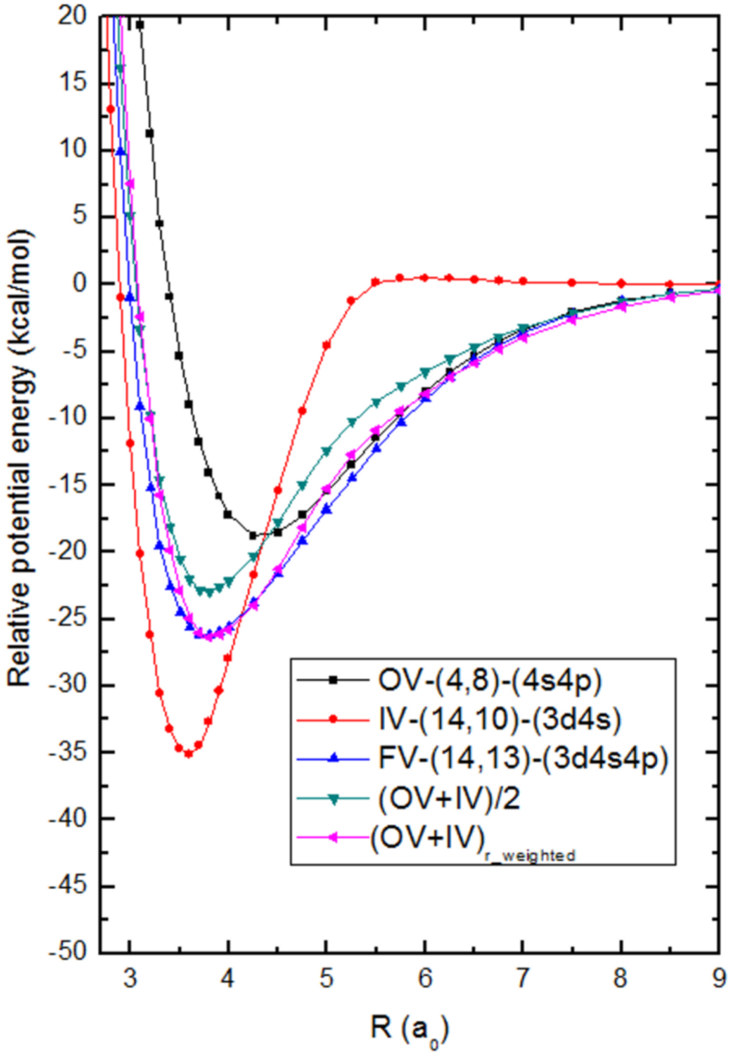
X $[1s^2]$ $\{2s^2 2p^{N_x}\}$

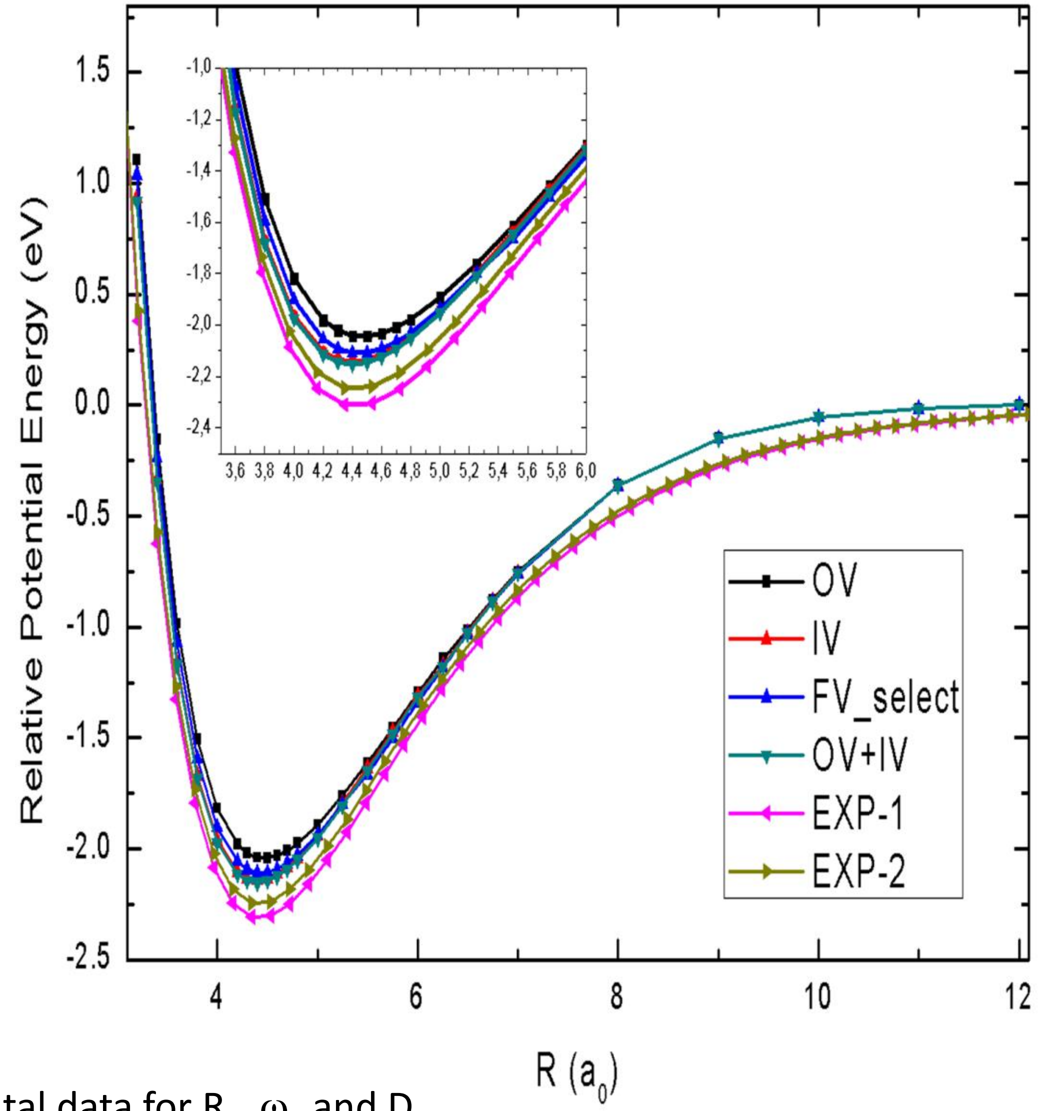
FV ~100,000 CFS

OV+IV ~900 CFS

J. Chem. Phys., **139**, 124316 (2013)

CuB, CuAl, CuB^+, $CuAl^+$



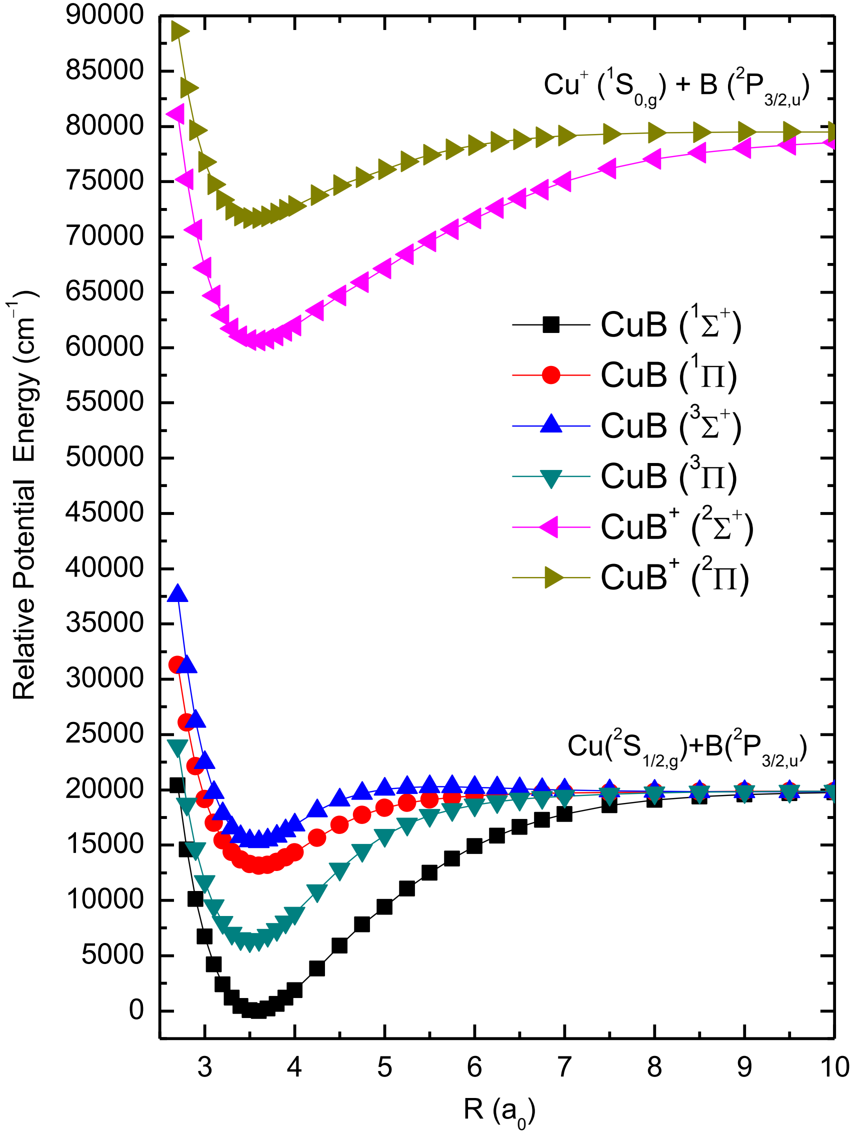


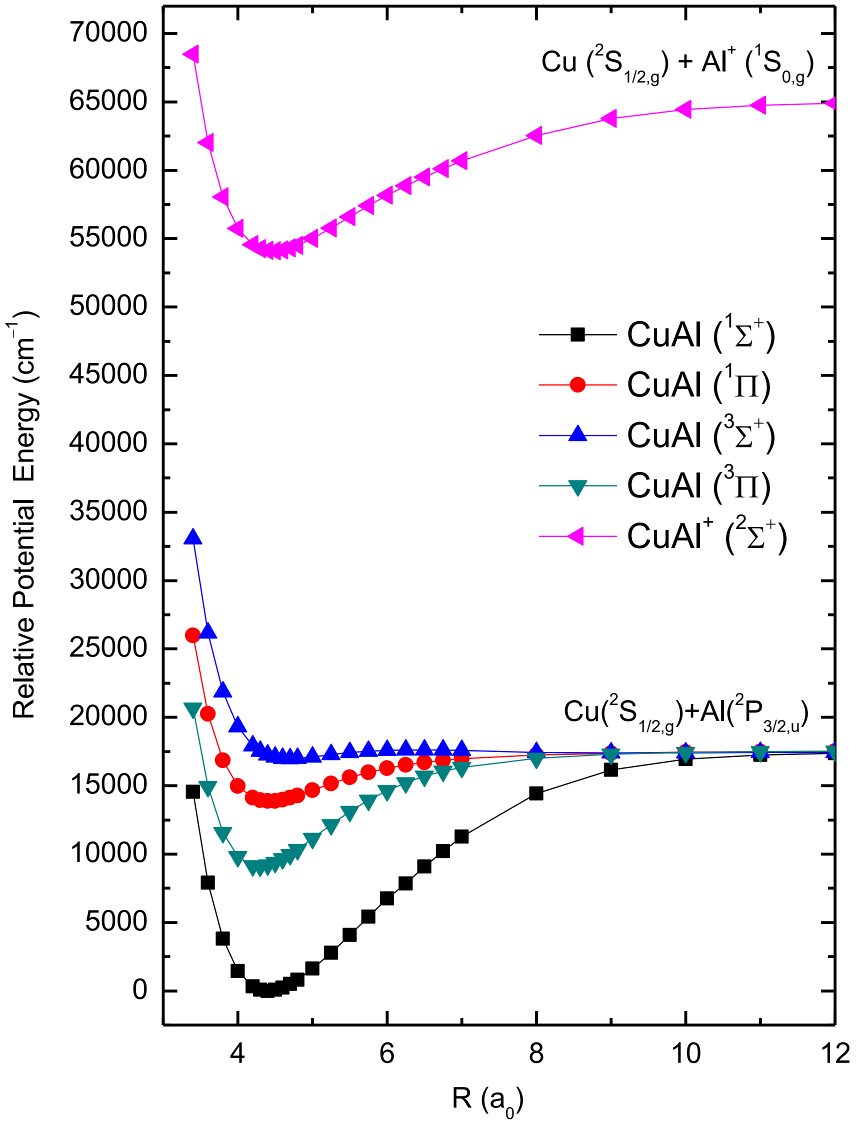
CuAl ($X - {}^1\Sigma^+$). Exp. Morse potential with experimental data for R_e, ω_e and D_e.

J. Chem. Phys., **139**, 124316 (2013)

CuB, CuAl, CuB^+, $CuAl^+$

CuB (left) and CuAl (right) potential energy curves obtained with MRCI+Q/A5Z





J. Chem. Phys., **139**, 124316 (2013)

CuB, CuAl, CuB^+, $CuAl^+$

Molecular constants of CuAl electronic ground state.

	Method	Reference set	T_e (cm^{-1})	R_e (a_0)	ω_e (cm^{-1})	$\omega_e\chi_e$ (cm^{-1})	D_0 (eV)
$(X)^1\Sigma^+$	MRCI+Q	OV	---	2.406	261	1.1	1.89
		IV	---	2.369	276	1.6	1.97
		OV+IV	---	2.369	275	1.4	1.98
		FV_select	---	2.389	264	0.5	1.94
	MRCI+Q+C.G	OV	---	2.363	277	1.3	2.03
		IV	---	2.329	293	1.7	2.13
		OV+IV	---	2.329	292	1.5	2.14
		FV_select	---	2.348	284	2.9	2.09
	Exp.*	---	---	2.339	294	---	2.3(15)

Molecular constants of CuAl first singlet excited state.

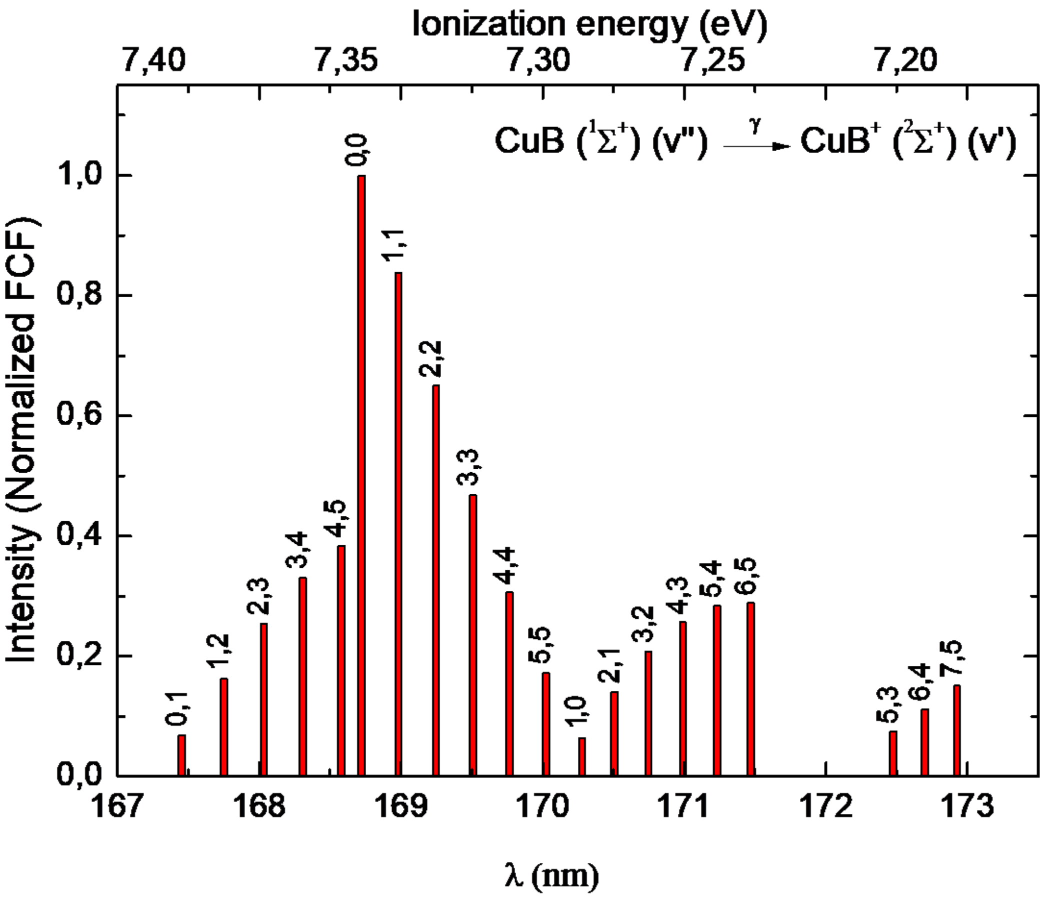
	Method	Reference set	T_e (cm^{-1})	R_e (a_0)	ω_e (cm^{-1})	$\omega_e\chi_e$ (cm^{-1})	D_0 (eV)
$(A)^1\Pi$	MRCI+Q	OV	13124	2.438	186	3.7	0.28
		IV	13227	2.408	200	1.6	0.35
		OV+IV	13238	2.389	209	3.3	0.37
		FV_select	13205	2.413	198	0.6	0.31
	MRCI+Q+C.G	OV	13726	2.382	206	3.6	0.35
		IV	14522	2.392	189	-0.9	0.35
		OV+IV	13865	2.338	229	3.4	0.44
		FV_select	13853	2.360	215	-1.1	0.38
	Exp.*	---	14892	2.353	224	---	0.4(7)

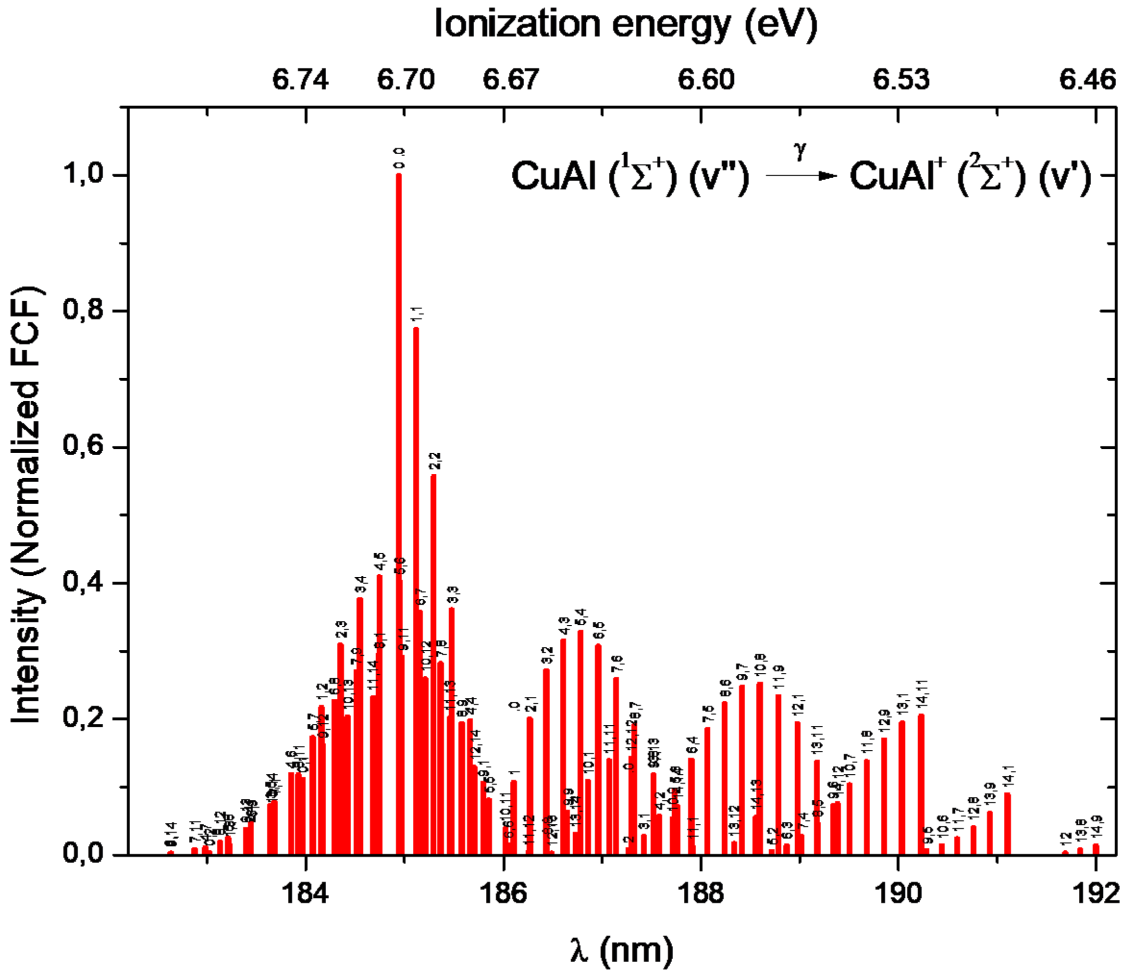
*J. M. Behm, C. A. Arrington, J. D. Langenberg and M. D. Morse *J. Chem. Phys.*, **99**, 6394 (1993).

J. Chem. Phys., **139**, 124316 (2013)

CuB, CuAl, CuB^+, $CuAl^+$

CuB (left) and CuAl (right) photoionization spectra.





J. Chem. Phys., **139**, 124316 (2013)

Applications : O_2

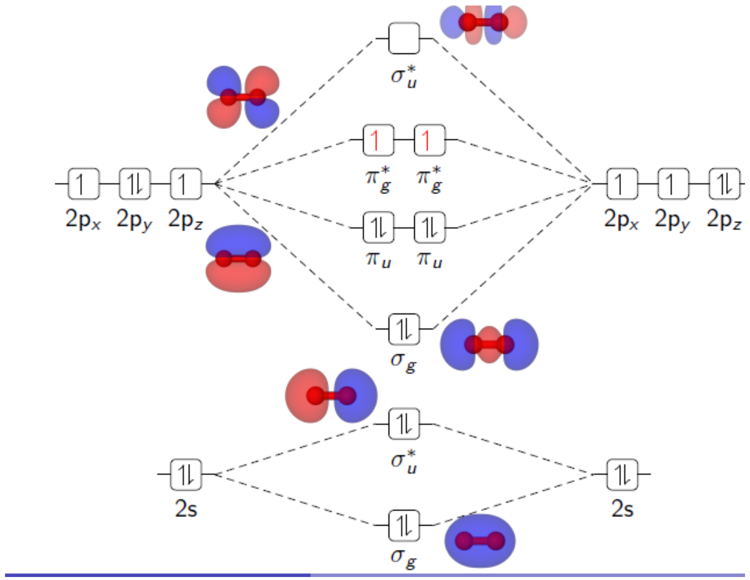
Exp.	R_e (A)	D_0 (cm^{-1})	T_e (cm^{-1})
$X^3\Sigma_g^-$	1.2075	41260	0.00
$A^3\Sigma_u^+$	1.5215	5862	35398

Previous Information?

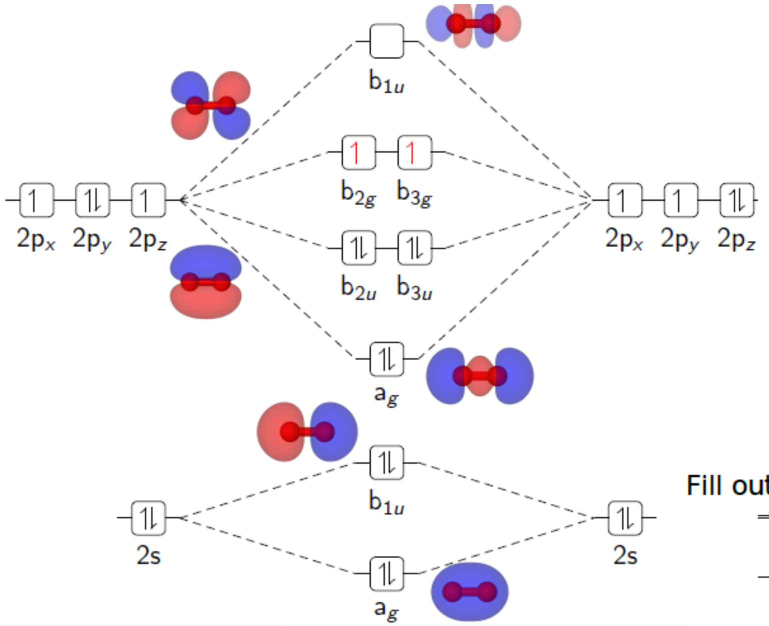
O: term symbol : ^3P_u

Exp. $^3\Sigma_g^-$

$D_{\infty h}$



D_{2h} $^3B_{1g}$



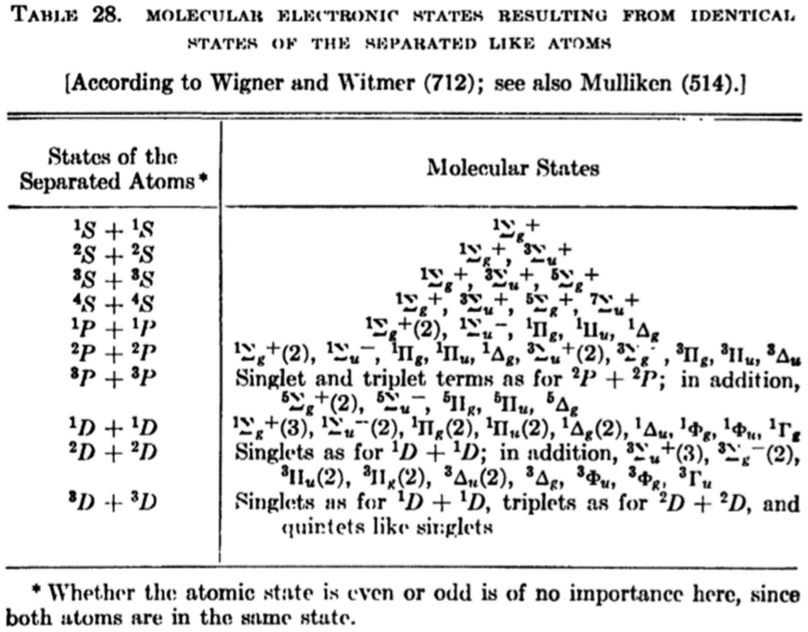


TABLE 28. MOLECULAR ELECTRONIC STATES RESULTING FROM IDENTICAL STATES OF THE SEPARATED LIKE ATOMS

[According to Wigner and Witmer (712); see also Mulliken (514).]

States of the Separated Atoms*	Molecular States
$^1S + {}^1S$	$^1\Sigma_g^+$
$^2S + {}^2S$	$^1\Sigma_g^+$, $^3\Sigma_u^+$
$^3S + {}^3S$	$^1\Sigma_g^+$, $^3\Sigma_u^+$, $^5\Sigma_g^+$
$^4S + {}^4S$	$^1\Sigma_g^+$, $^3\Sigma_u^+$, $^5\Sigma_g^+$, $^7\Sigma_u^+$
$^1P + {}^1P$	$^1\Sigma_g^+(2)$, $^1\Sigma_u^-$, $^1\Pi_g$, $^1\Pi_u$, $^1\Delta_g$
$^2P + {}^2P$	$^1\Sigma_g^+(2)$, $^1\Sigma_u^-$, $^1\Pi_g$, $^1\Pi_u$, $^1\Delta_g$, $^3\Sigma_u^+(2)$, $^3\Sigma_g^-$, $^3\Pi_g$, $^3\Pi_u$, $^3\Delta_u$
$^3P + {}^3P$	Singlet and triplet terms as for $^2P + {}^2P$; in addition, $^5\Sigma_g^+(2)$, $^5\Sigma_u^-$, $^5\Pi_g$, $^5\Pi_u$, $^5\Delta_g$
$^1D + {}^1D$	$^1\Sigma_g^+(3)$, $^1\Sigma_u^-(2)$, $^1\Pi_g(2)$, $^1\Pi_u(2)$, $^1\Delta_g(2)$, $^1\Delta_u$, $^1\Phi_g$, $^1\Phi_u$, $^1\Gamma_g$
$^2D + {}^2D$	Singlets as for $^1D + {}^1D$; in addition, $^3\Sigma_u^+(3)$, $^3\Sigma_g^-(2)$, $^3\Pi_u(2)$, $^3\Pi_g(2)$, $^3\Delta_u(2)$, $^3\Delta_g$, $^3\Phi_u$, $^3\Phi_g$, $^3\Gamma_u$
$^3D + {}^3D$	Singlets as for $^1D + {}^1D$, triplets as for $^2D + {}^2D$, and quintets like singlets

* Whether the atomic state is even or odd is of no importance here, since both atoms are in the same state.

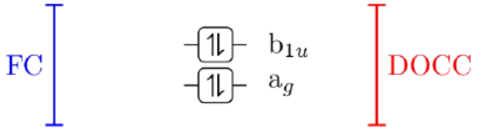
Potential curves for 2 states

Fill out the DRT table.

State	Multiplicity	N. electrons	Symmetry
1	3	16	B_{1g}
1	3	16	B_{1u}
Number of distinct rows tables (DRTs):			2

HF: $1a_g^2 1b_{1u}^2 2a_g^2 2b_{1u}^2 3a_g^2 1b_{2u}^2 1b_{3u}^2 1b_{2g}^1 1b_{3g}^1 3b_{1u}^0$

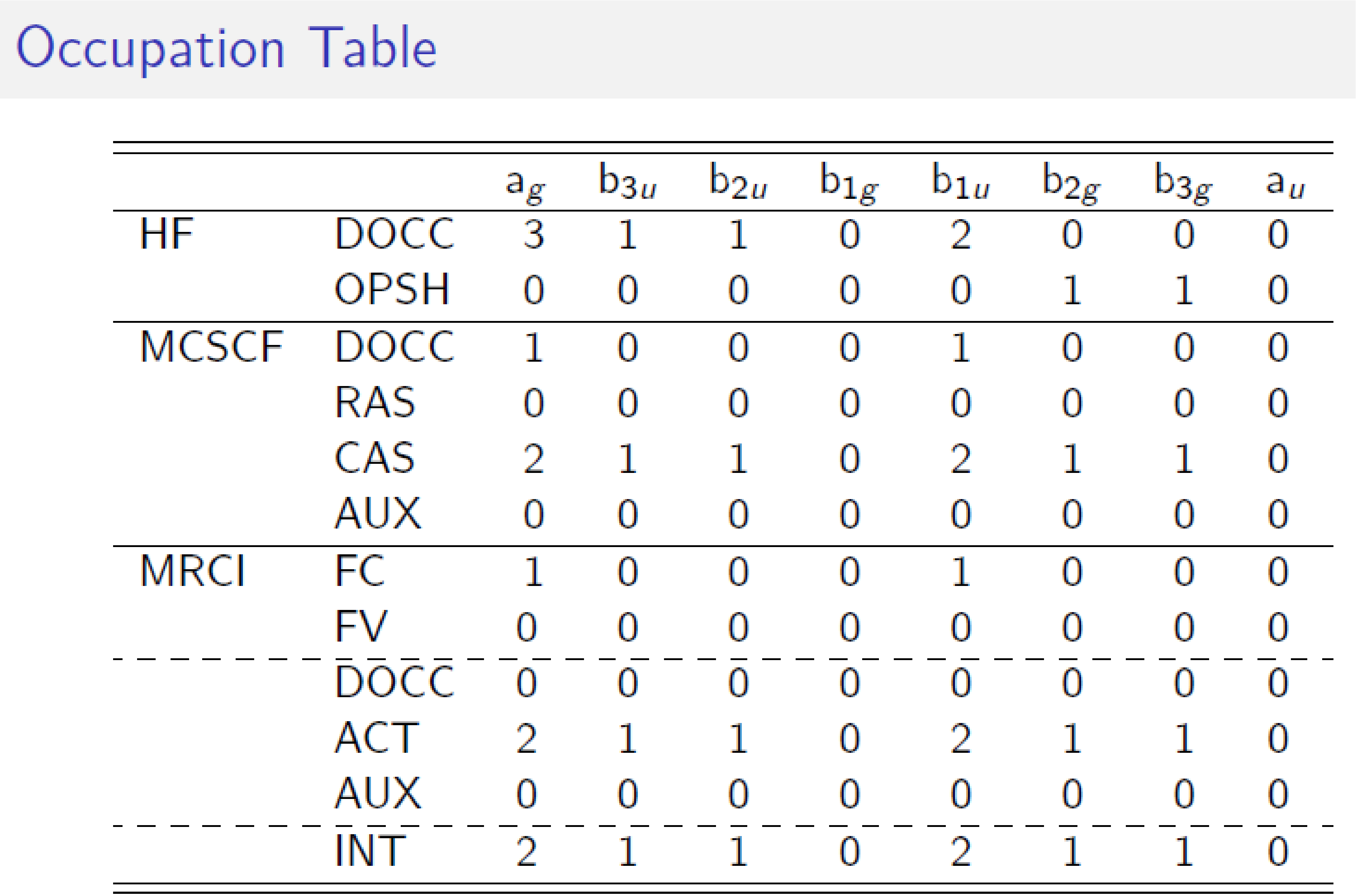
Basis set: 6-31G*



Active Space: valence

CAS(12,8) = $2a_g 2b_{1u} 1b_{2u} 1b_{3u} 1b_{2g} 1b_{3g}$

Applications : O_2



Occupation Table

		a_g	b_{3u}	b_{2u}	b_{1g}	b_{1u}	b_{2g}	b_{3g}	a_u
HF	DOCC	3	1	1	0	2	0	0	0
	OPSH	0	0	0	0	0	1	1	0
MCSCF	DOCC	1	0	0	0	1	0	0	0
	RAS	0	0	0	0	0	0	0	0
	CAS	2	1	1	0	2	1	1	0
	AUX	0	0	0	0	0	0	0	0
MRCI	FC	1	0	0	0	1	0	0	0
	FV	0	0	0	0	0	0	0	0
	DOCC	0	0	0	0	0	0	0	0
	ACT	2	1	1	0	2	1	1	0
	AUX	0	0	0	0	0	0	0	0
	INT	2	1	1	0	2	1	1	0

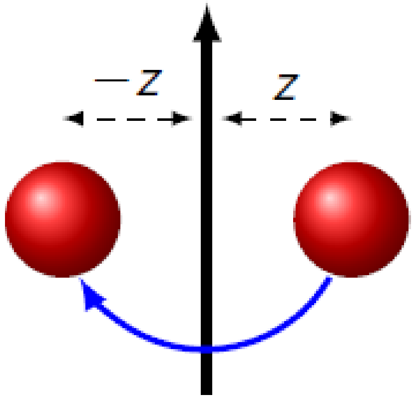
Applications : O_2

Coordinates

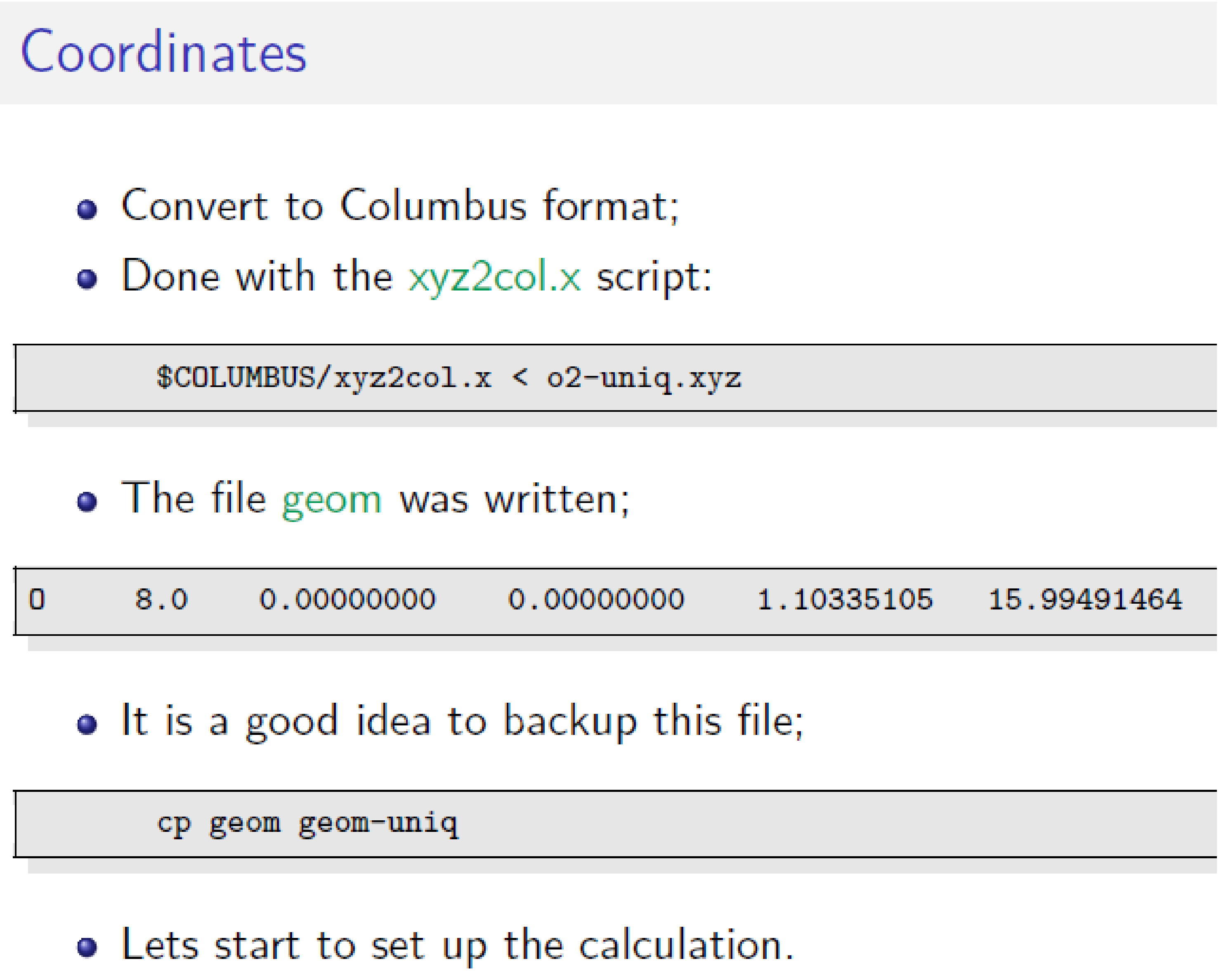
- Write the XYZ file;
- Only the unique atoms are required.

```
1
Row 1 - # of atoms. from row 3 - Atom symbol and XYZ coordinates.
O     0.000000     0.000000     0.583868
```

- The other atom will be created by symmetry operations:



Applications : O_2



Coordinates

- Convert to Columbus format;
- Done with the xyz2col.x script:

```
$COLUMBUS/xyz2col.x < o2-uniq.xyz
```

- The file geom was written;

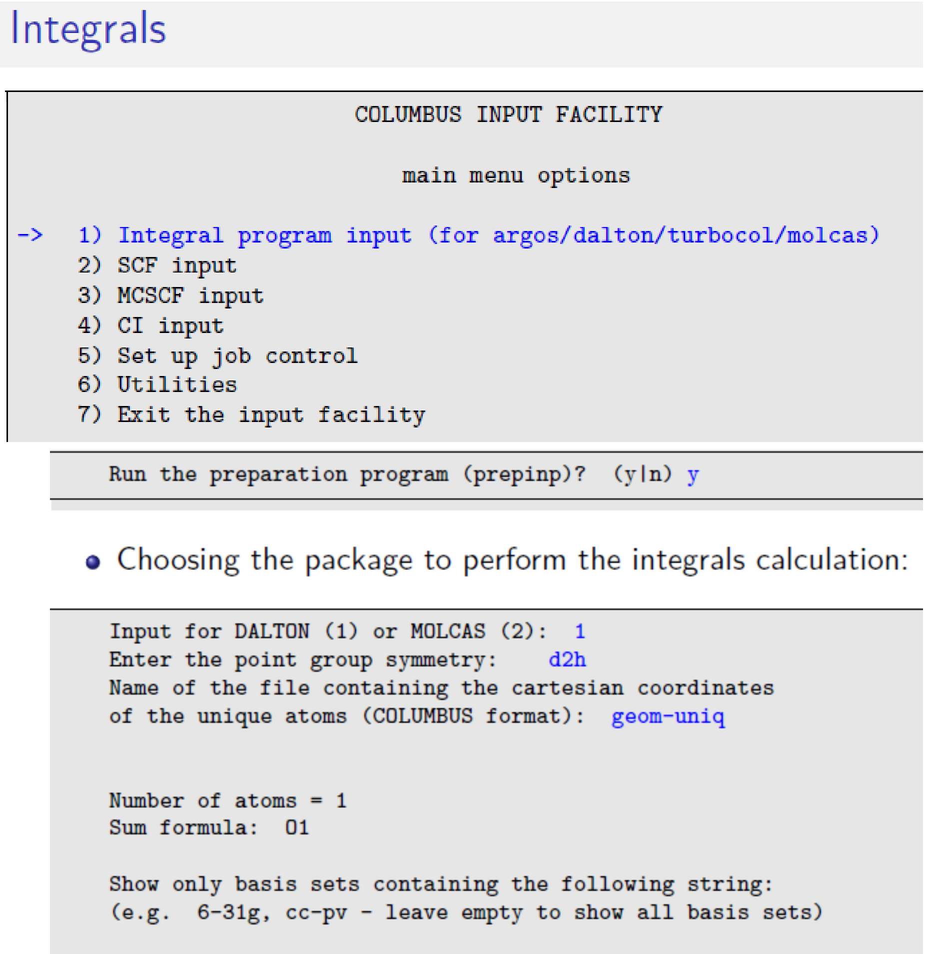
```
O       8.0      0.00000000      0.00000000      1.10335105    15.99491464
```

- It is a good idea to backup this file;

```
cp geom geom-uniq
```

- Lets start to set up the calculation.

Applications : O_2



Integrals

```
                    COLUMBUS INPUT FACILITY

                       main menu options

->  1) Integral program input (for argos/dalton/turbocol/molcas)
    2) SCF input
    3) MCSCF input
    4) CI input
    5) Set up job control
    6) Utilities
    7) Exit the input facility
```

```
   Run the preparation program (prepinp)?  (y|n) y
```

- Choosing the package to perform the integrals calculation:

```
   Input for DALTON (1) or MOLCAS (2):  1
   Enter the point group symmetry:    d2h
   Name of the file containing the cartesian coordinates
   of the unique atoms (COLUMBUS format):  geom-uniq


   Number of atoms = 1
   Sum formula:  O1

   Show only basis sets containing the following string:
   (e.g.  6-31g, cc-pv - leave empty to show all basis sets)
```

34: OXYGEN Pople 6-31g* or 6-31g**

Select the basis set for atom O: 34 ! *6-31g* was selected*

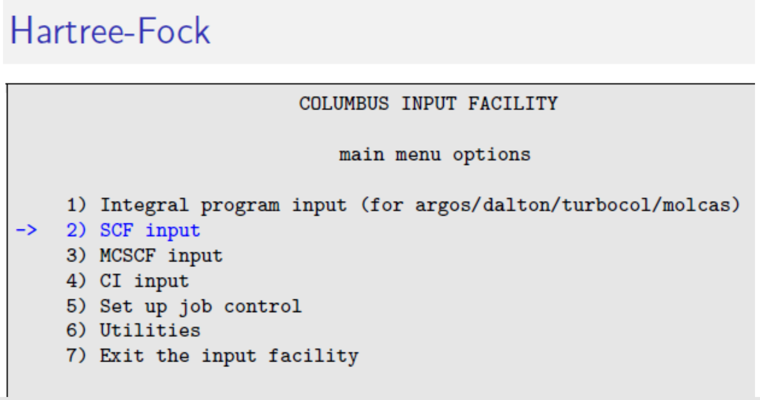
…

Until now you've set the following basis sets:

O :: OXYGEN Pople 6-31g* or 6-31g**

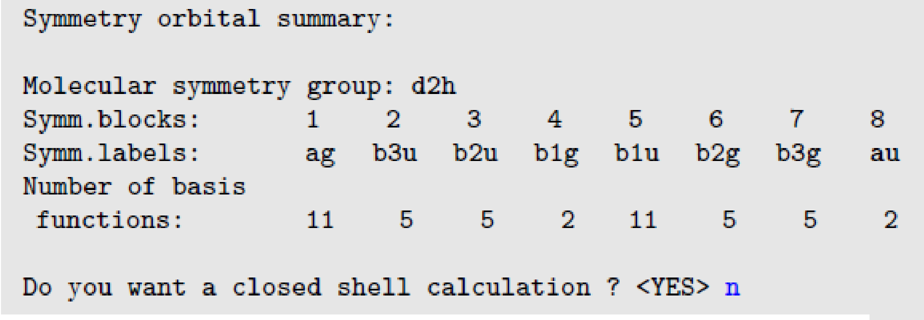
Reorder geom file for geometry optimization and orbital print out? (y) y ! *per default the geometry should be reordered to put the hydrogens at the back of the file.*

Would you like to do an interactive input? <NO> n ! *Select "no".*

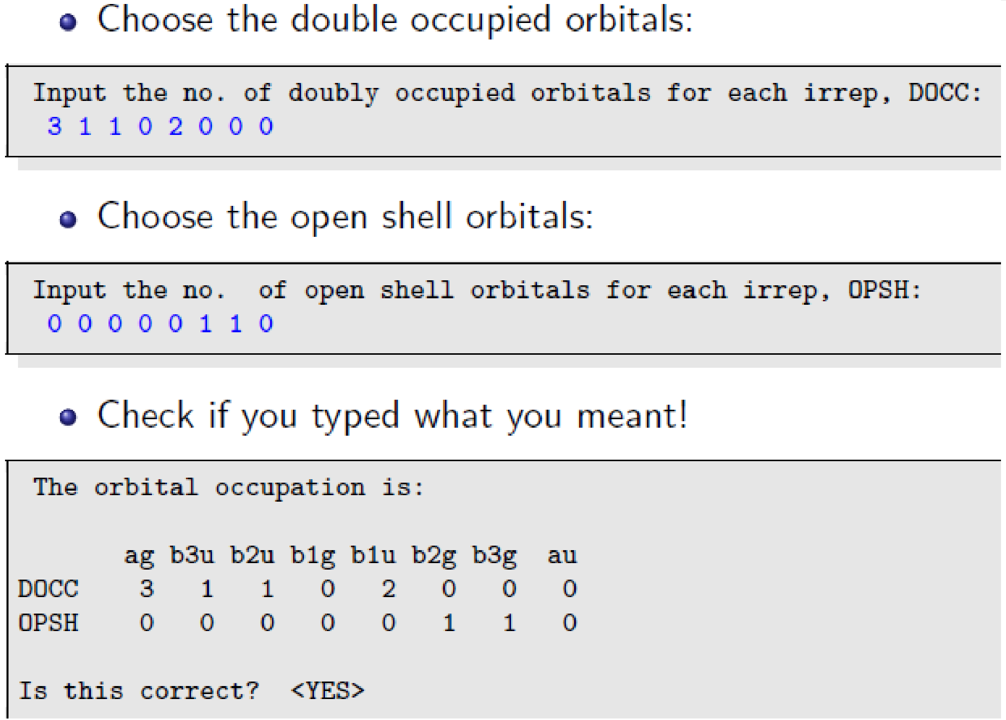


Hartree-Fock

```
                    COLUMBUS INPUT FACILITY

                       main menu options

    1) Integral program input (for argos/dalton/turbocol/molcas)
->  2) SCF input
    3) MCSCF input
    4) CI input
    5) Set up job control
    6) Utilities
    7) Exit the input facility
```



```
Symmetry orbital summary:

Molecular symmetry group: d2h
Symm.blocks:         1     2     3     4     5     6     7     8
Symm.labels:        ag   b3u   b2u   b1g   b1u   b2g   b3g    au
Number of basis
 functions:         11     5     5     2    11     5     5     2

Do you want a closed shell calculation ? <YES> n
```



- Choose the double occupied orbitals:

```
 Input the no. of doubly occupied orbitals for each irrep, DOCC:
  3 1 1 0 2 0 0 0
```

- Choose the open shell orbitals:

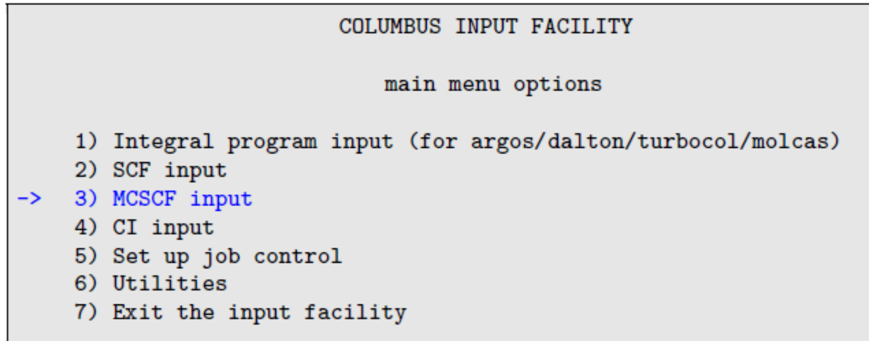
```
 Input the no.  of open shell orbitals for each irrep, OPSH:
  0 0 0 0 0 1 1 0
```

- Check if you typed what you meant!

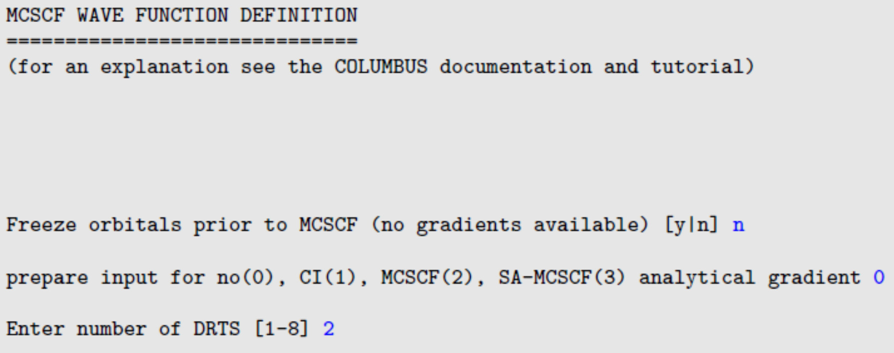
```
 The orbital occupation is:

       ag b3u b2u b1g b1u b2g b3g  au
DOCC    3   1   1   0   2   0   0   0
OPSH    0   0   0   0   0   1   1   0

Is this correct?  <YES>
```

Applications : O_2

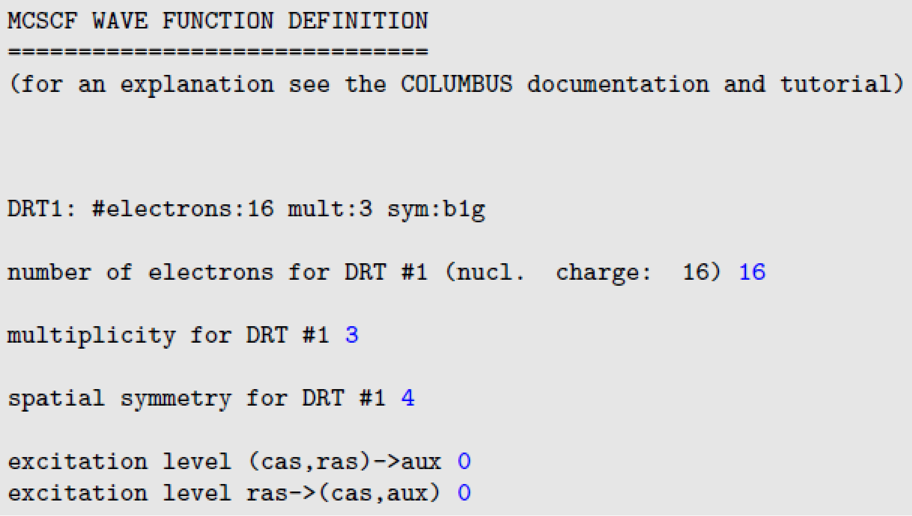
MCSCF



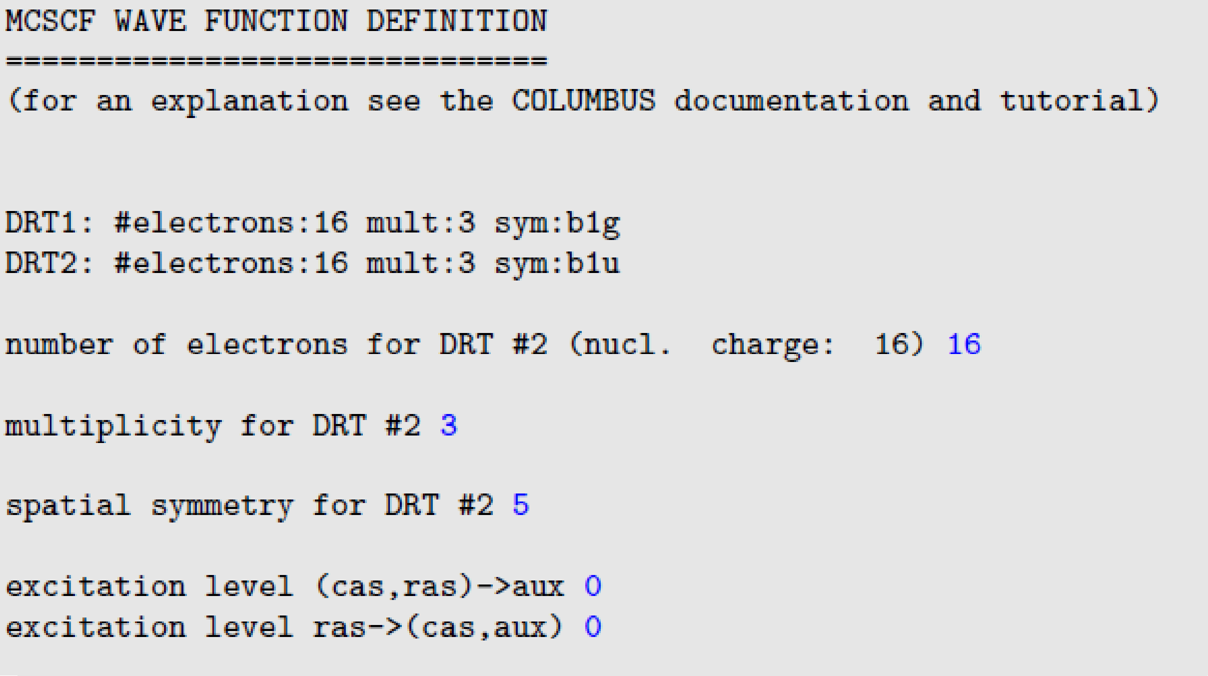
```
                    COLUMBUS INPUT FACILITY

                       main menu options

     1) Integral program input (for argos/dalton/turbocol/molcas)
     2) SCF input
->   3) MCSCF input
     4) CI input
     5) Set up job control
     6) Utilities
     7) Exit the input facility
```



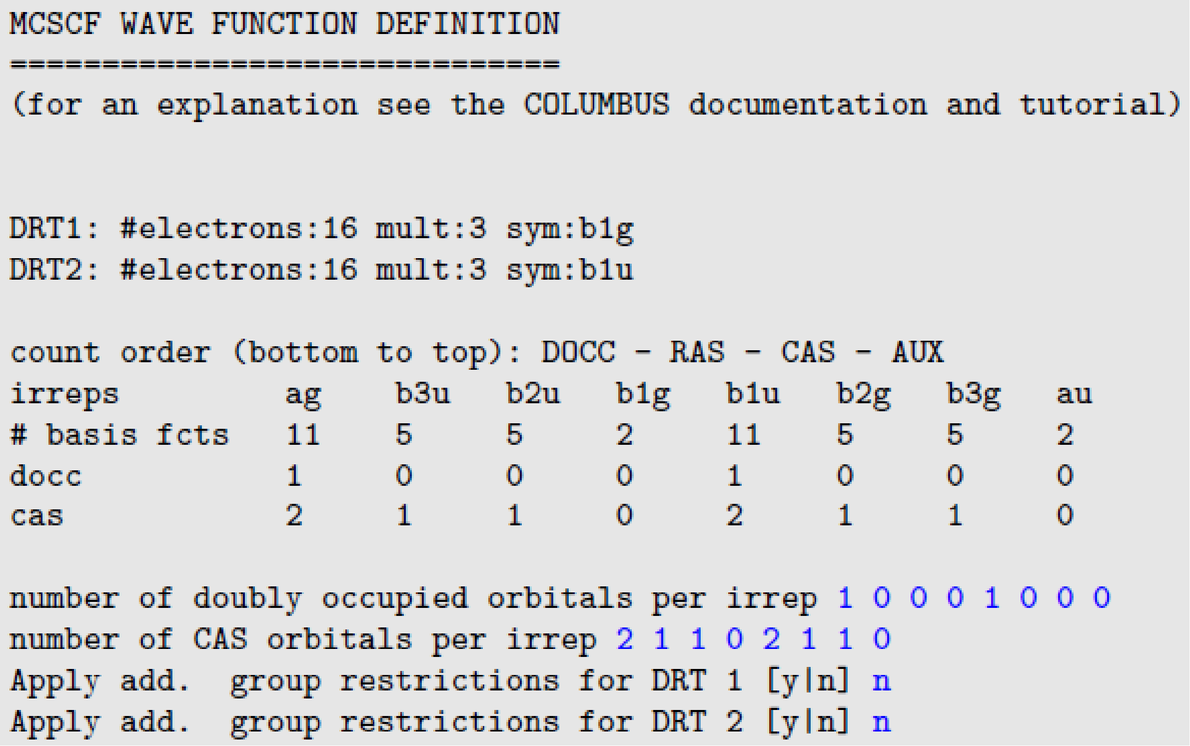
```
MCSCF WAVE FUNCTION DEFINITION
==============================
(for an explanation see the COLUMBUS documentation and tutorial)




Freeze orbitals prior to MCSCF (no gradients available) [y|n] n

prepare input for no(0), CI(1), MCSCF(2), SA-MCSCF(3) analytical gradient 0

Enter number of DRTS [1-8] 2
```



```
MCSCF WAVE FUNCTION DEFINITION
==============================
(for an explanation see the COLUMBUS documentation and tutorial)


DRT1: #electrons:16 mult:3 sym:b1g

number of electrons for DRT #1 (nucl.  charge:  16) 16

multiplicity for DRT #1 3

spatial symmetry for DRT #1 4

excitation level (cas,ras)->aux 0
excitation level ras->(cas,aux) 0
```

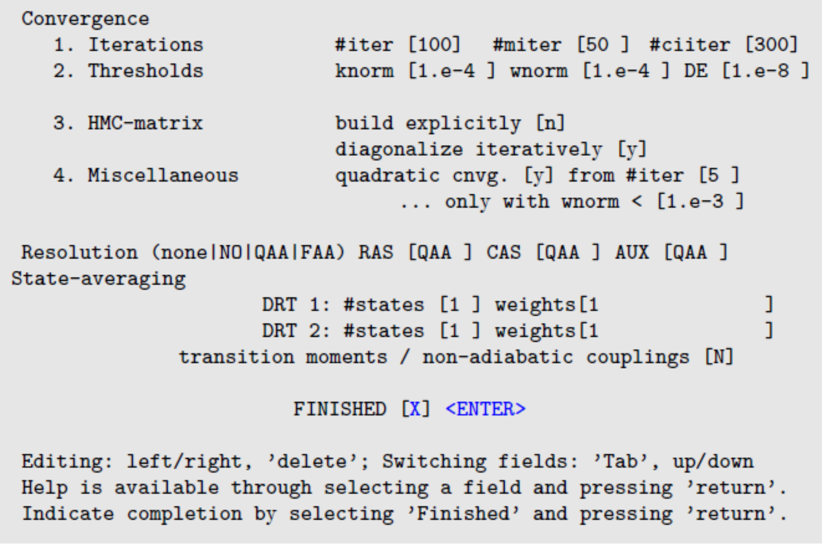


```
MCSCF WAVE FUNCTION DEFINITION
==============================
(for an explanation see the COLUMBUS documentation and tutorial)


DRT1: #electrons:16 mult:3 sym:b1g
DRT2: #electrons:16 mult:3 sym:b1u

number of electrons for DRT #2 (nucl.  charge:  16) 16

multiplicity for DRT #2 3

spatial symmetry for DRT #2 5

excitation level (cas,ras)->aux 0
excitation level ras->(cas,aux) 0
```



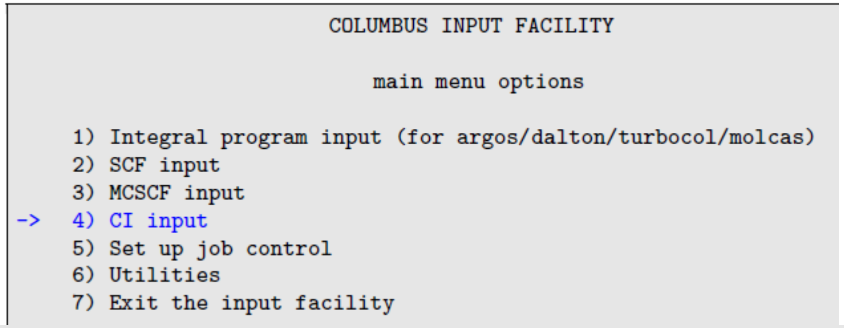
```
MCSCF WAVE FUNCTION DEFINITION
==============================
(for an explanation see the COLUMBUS documentation and tutorial)


DRT1: #electrons:16 mult:3 sym:b1g
DRT2: #electrons:16 mult:3 sym:b1u

count order (bottom to top): DOCC - RAS - CAS - AUX
irreps         ag   b3u  b2u  b1g  b1u  b2g  b3g  au
# basis fcts   11   5    5    2    11   5    5    2
docc           1    0    0    0    1    0    0    0
cas            2    1    1    0    2    1    1    0

number of doubly occupied orbitals per irrep 1 0 0 0 1 0 0 0
number of CAS orbitals per irrep 2 1 1 0 2 1 1 0
Apply add.  group restrictions for DRT 1 [y|n] n
Apply add.  group restrictions for DRT 2 [y|n] n
```

Applications : O_2

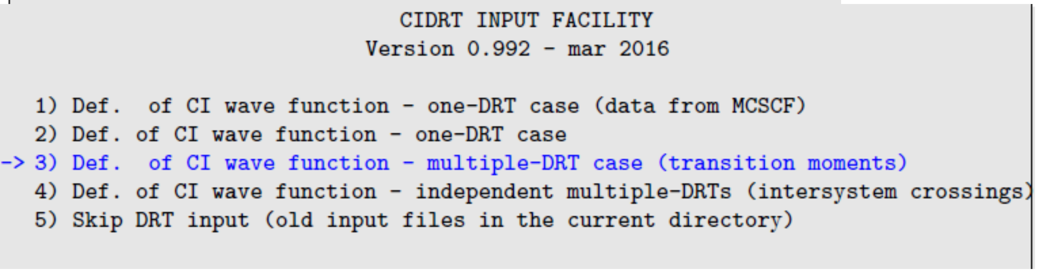


```
 Convergence
    1. Iterations            #iter [100]   #miter [50 ]  #ciiter [300]
    2. Thresholds            knorm [1.e-4 ] wnorm [1.e-4 ] DE [1.e-8 ]

    3. HMC-matrix            build explicitly [n]
                             diagonalize iteratively [y]
    4. Miscellaneous         quadratic cnvg. [y] from #iter [5 ]
                                  ... only with wnorm < [1.e-3 ]

 Resolution (none|NO|QAA|FAA) RAS [QAA ] CAS [QAA ] AUX [QAA ]
State-averaging
                       DRT 1: #states [1 ] weights[1              ]
                       DRT 2: #states [1 ] weights[1              ]
                transition moments / non-adiabatic couplings [N]

                           FINISHED [X] <ENTER>

 Editing: left/right, 'delete'; Switching fields: 'Tab', up/down
 Help is available through selecting a field and pressing 'return'.
 Indicate completion by selecting 'Finished' and pressing 'return'.
```

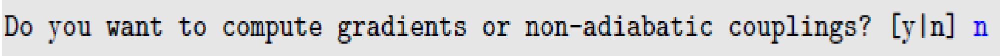
MRCI



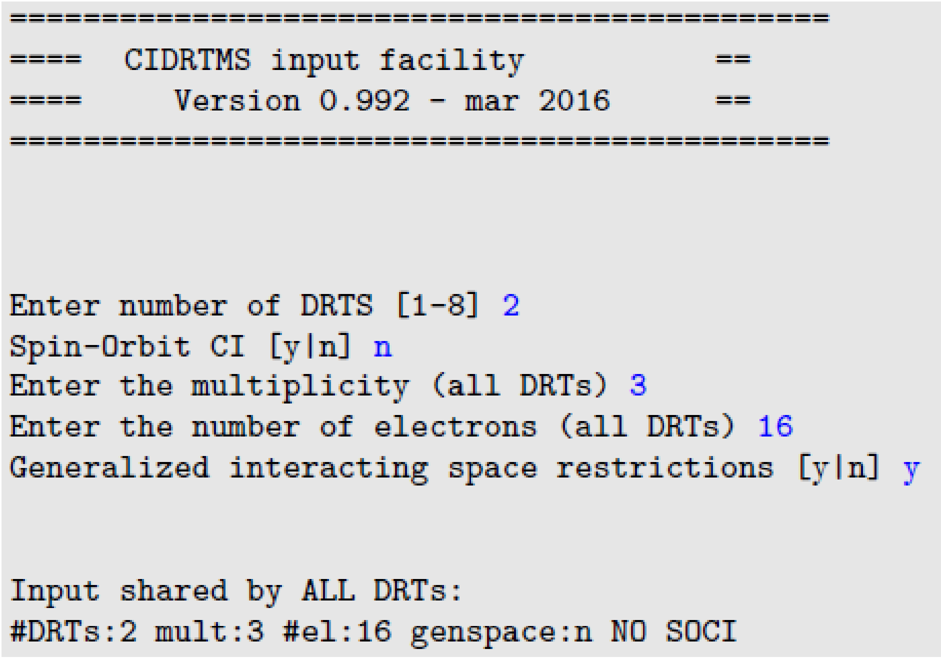
```
                         COLUMBUS INPUT FACILITY

                            main menu options

     1) Integral program input (for argos/dalton/turbocol/molcas)
     2) SCF input
     3) MCSCF input
 ->  4) CI input
     5) Set up job control
     6) Utilities
     7) Exit the input facility
```



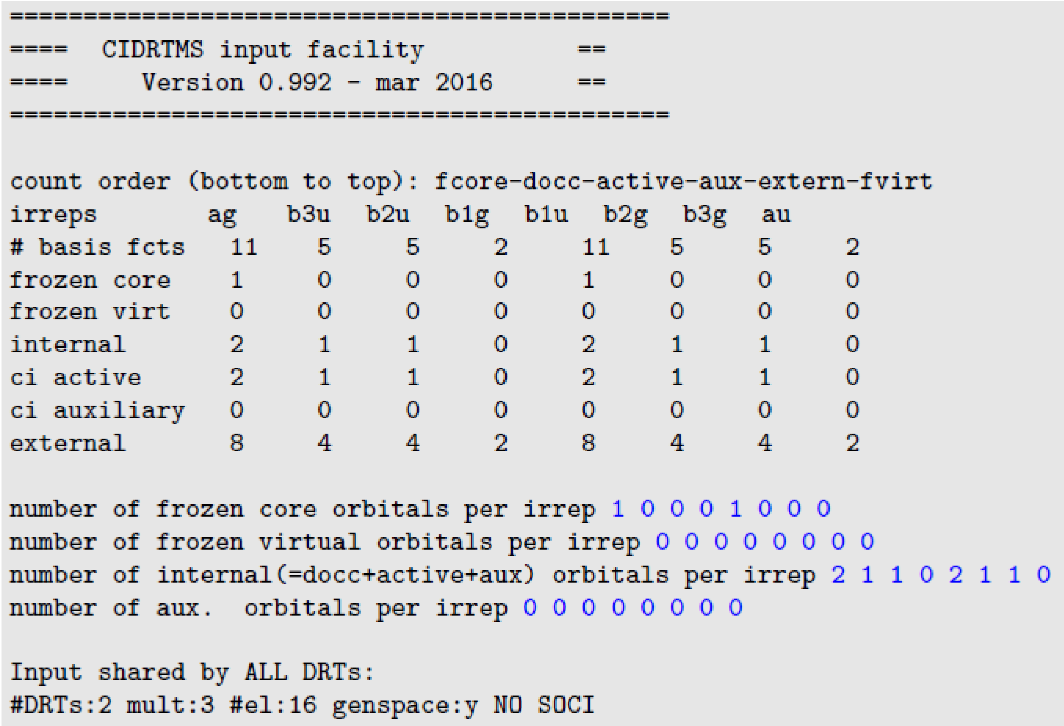
```
                        CIDRT INPUT FACILITY
                      Version 0.992 - mar 2016

  1) Def.  of CI wave function - one-DRT case (data from MCSCF)
  2) Def. of CI wave function - one-DRT case
-> 3) Def.  of CI wave function - multiple-DRT case (transition moments)
  4) Def. of CI wave function - independent multiple-DRTs (intersystem crossings)
  5) Skip DRT input (old input files in the current directory)
```



```
Do you want to compute gradients or non-adiabatic couplings? [y|n] n
```

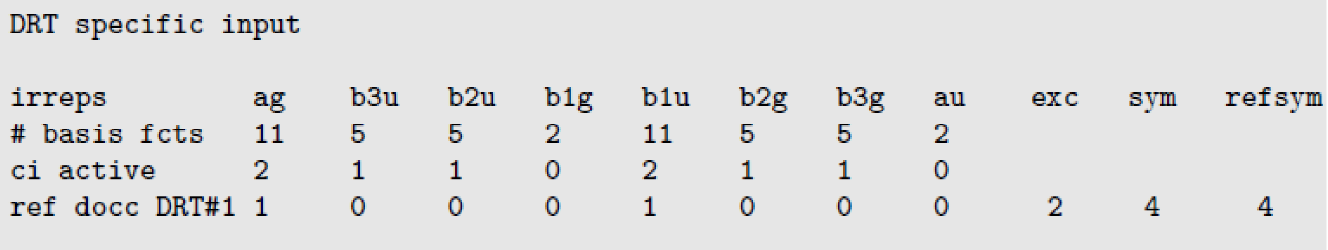


```
==========================================
====   CIDRTMS input facility           ==
====      Version 0.992 - mar 2016      ==
==========================================



Enter number of DRTS [1-8] 2
Spin-Orbit CI [y|n] n
Enter the multiplicity (all DRTs) 3
Enter the number of electrons (all DRTs) 16
Generalized interacting space restrictions [y|n] y


Input shared by ALL DRTs:
#DRTs:2 mult:3 #el:16 genspace:n NO SOCI
```

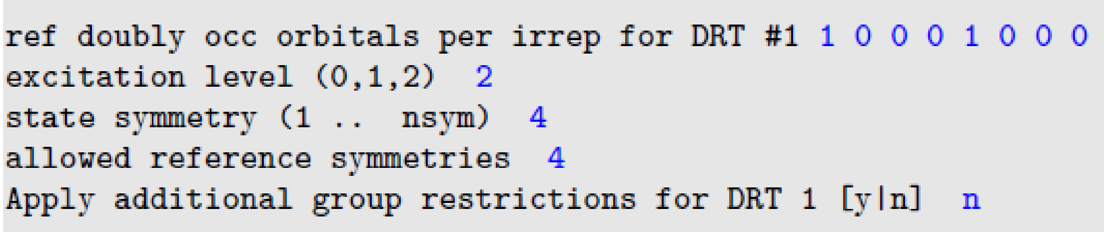


```
==========================================
====   CIDRTMS input facility           ==
====      Version 0.992 - mar 2016      ==
==========================================

count order (bottom to top): fcore-docc-active-aux-extern-fvirt
irreps          ag   b3u   b2u   b1g   b1u   b2g   b3g   au
# basis fcts     11     5     5     2    11     5     5     2
frozen core       1     0     0     0     1     0     0     0
frozen virt       0     0     0     0     0     0     0     0
internal          2     1     1     0     2     1     1     0
ci active         2     1     1     0     2     1     1     0
ci auxiliary      0     0     0     0     0     0     0     0
external          8     4     4     2     8     4     4     2

number of frozen core orbitals per irrep 1 0 0 0 1 0 0 0
number of frozen virtual orbitals per irrep 0 0 0 0 0 0 0 0
number of internal(=docc+active+aux) orbitals per irrep 2 1 1 0 2 1 1 0
number of aux.  orbitals per irrep 0 0 0 0 0 0 0 0

Input shared by ALL DRTs:
#DRTs:2 mult:3 #el:16 genspace:y NO SOCI
```

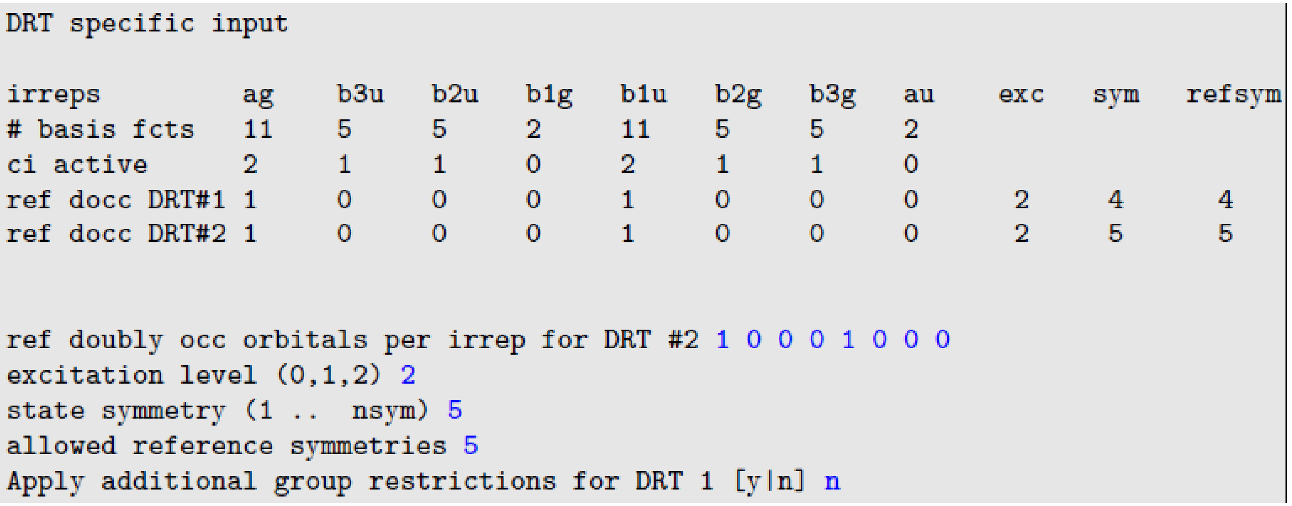
Applications : O_2



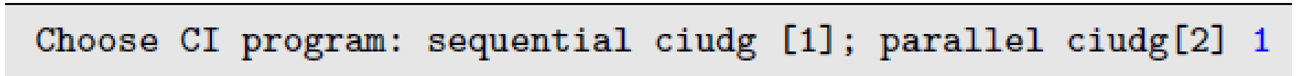
```
DRT specific input

irreps          ag    b3u   b2u   b1g   b1u   b2g   b3g   au     exc    sym    refsym
# basis fcts    11    5     5     2     11    5     5     2
ci active       2     1     1     0     2     1     1     0
ref docc DRT#1  1     0     0     0     1     0     0     0       2      4       4
```



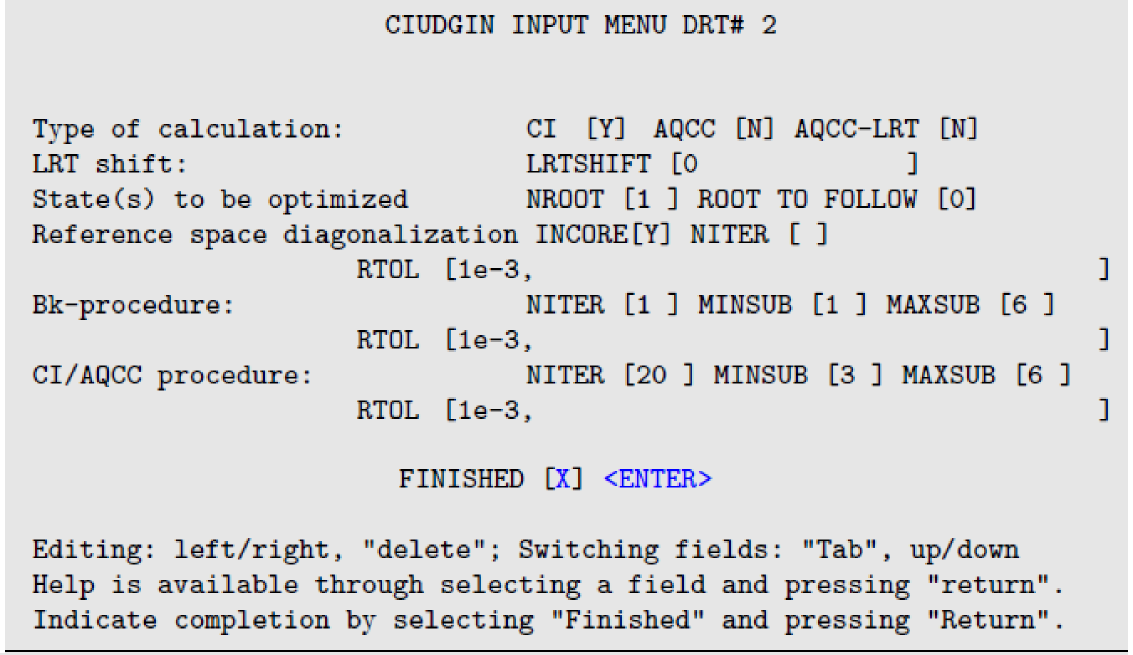
```
ref doubly occ orbitals per irrep for DRT #1 1 0 0 0 1 0 0 0
excitation level (0,1,2)  2
state symmetry (1 ..  nsym)  4
allowed reference symmetries  4
Apply additional group restrictions for DRT 1 [y|n]  n
```



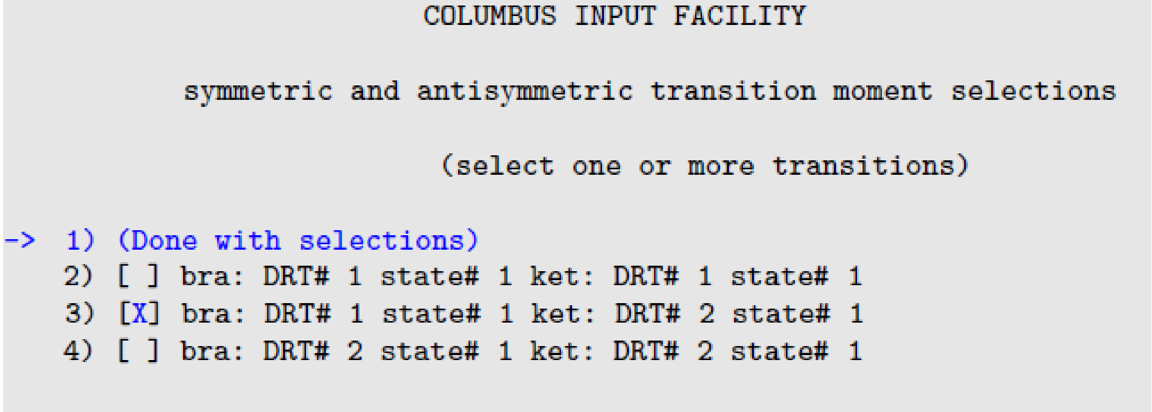
```
DRT specific input

irreps          ag    b3u   b2u   b1g   b1u   b2g   b3g   au     exc    sym    refsym
# basis fcts    11    5     5     2     11    5     5     2
ci active       2     1     1     0     2     1     1     0
ref docc DRT#1  1     0     0     0     1     0     0     0       2      4       4
ref docc DRT#2  1     0     0     0     1     0     0     0       2      5       5


ref doubly occ orbitals per irrep for DRT #2 1 0 0 0 1 0 0 0
excitation level (0,1,2) 2
state symmetry (1 ..  nsym) 5
allowed reference symmetries 5
Apply additional group restrictions for DRT 1 [y|n] n
```



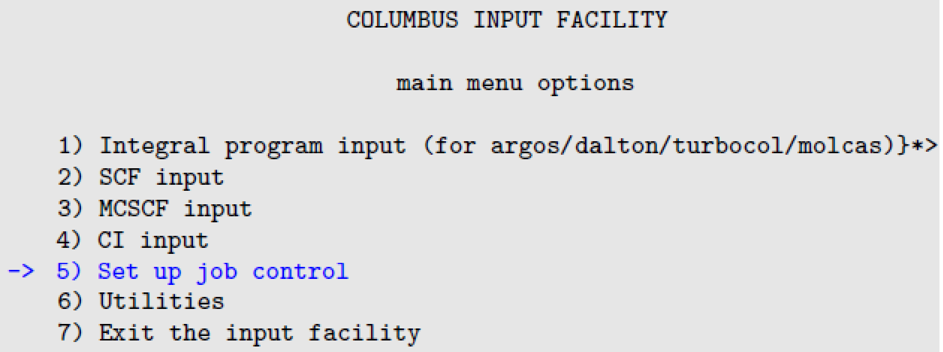
```
Choose CI program: sequential ciudg [1]; parallel ciudg[2] 1
```



```
                          CIUDGIN INPUT MENU DRT# 2


Type of calculation:                CI  [Y]  AQCC [N] AQCC-LRT [N]
LRT shift:                          LRTSHIFT [0                  ]
State(s) to be optimized            NROOT [1 ] ROOT TO FOLLOW [0]
Reference space diagonalization INCORE[Y] NITER [ ]
                         RTOL  [1e-3,                                   ]
Bk-procedure:                       NITER [1 ] MINSUB [1 ] MAXSUB [6 ]
                         RTOL  [1e-3,                                   ]
CI/AQCC procedure:                  NITER [20 ] MINSUB [3 ] MAXSUB [6 ]
                         RTOL  [1e-3,                                   ]

                          FINISHED [X] <ENTER>

Editing: left/right, "delete"; Switching fields: "Tab", up/down
Help is available through selecting a field and pressing "return".
Indicate completion by selecting "Finished" and pressing "Return".
```

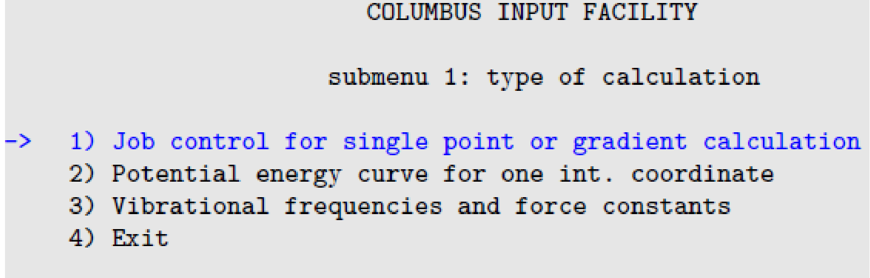


```
                        COLUMBUS INPUT FACILITY

        symmetric and antisymmetric transition moment selections

                     (select one or more transitions)

->  1) (Done with selections)
    2) [ ] bra: DRT# 1 state# 1 ket: DRT# 1 state# 1
    3) [X] bra: DRT# 1 state# 1 ket: DRT# 2 state# 1
    4) [ ] bra: DRT# 2 state# 1 ket: DRT# 2 state# 1
```

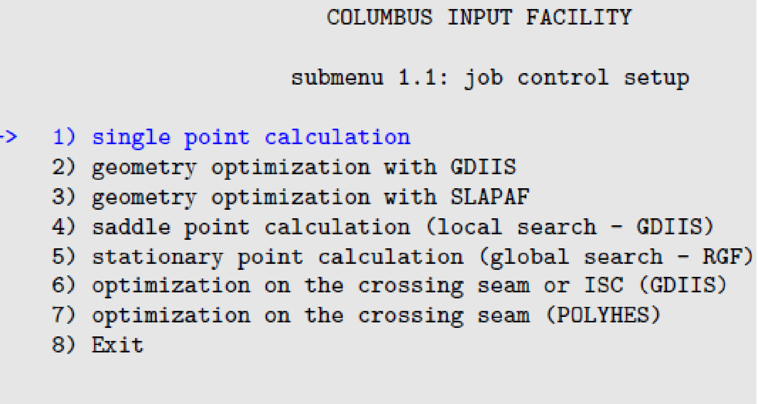


```
                       COLUMBUS INPUT FACILITY

                         main menu options

    1) Integral program input (for argos/dalton/turbocol/molcas)}*>
    2) SCF input
    3) MCSCF input
    4) CI input
->  5) Set up job control
    6) Utilities
    7) Exit the input facility
```

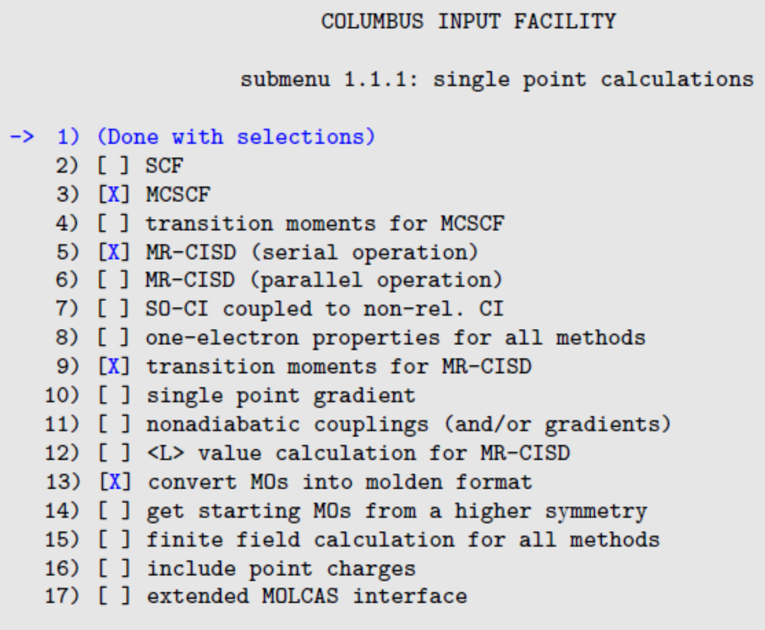
Applications : O_2



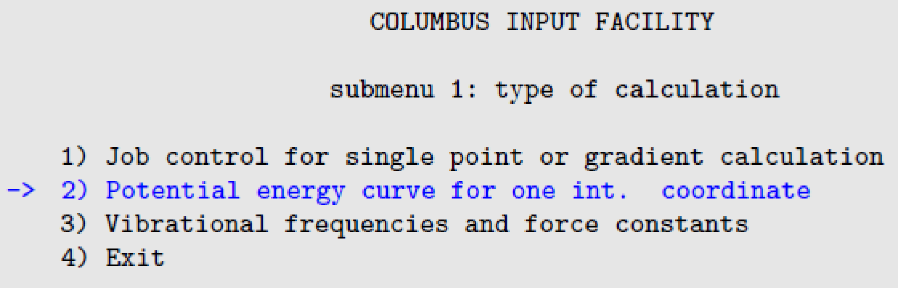
```
                    COLUMBUS INPUT FACILITY

                 submenu 1: type of calculation

->   1) Job control for single point or gradient calculation
     2) Potential energy curve for one int. coordinate
     3) Vibrational frequencies and force constants
     4) Exit
```



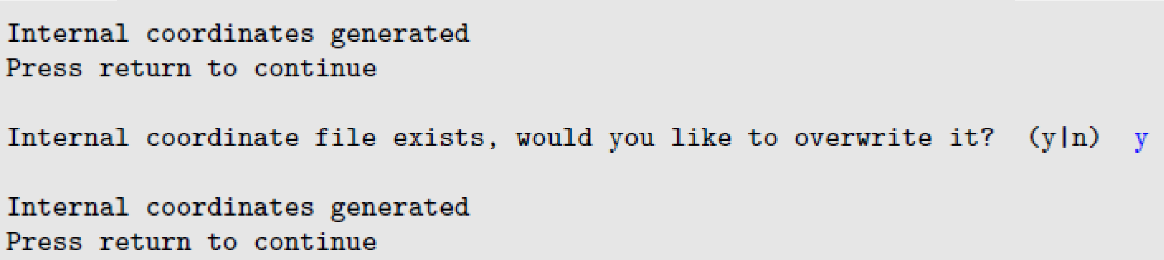
```
                 COLUMBUS INPUT FACILITY

              submenu 1.1: job control setup

->   1) single point calculation
     2) geometry optimization with GDIIS
     3) geometry optimization with SLAPAF
     4) saddle point calculation (local search - GDIIS)
     5) stationary point calculation (global search - RGF)
     6) optimization on the crossing seam or ISC (GDIIS)
     7) optimization on the crossing seam (POLYHES)
     8) Exit
```



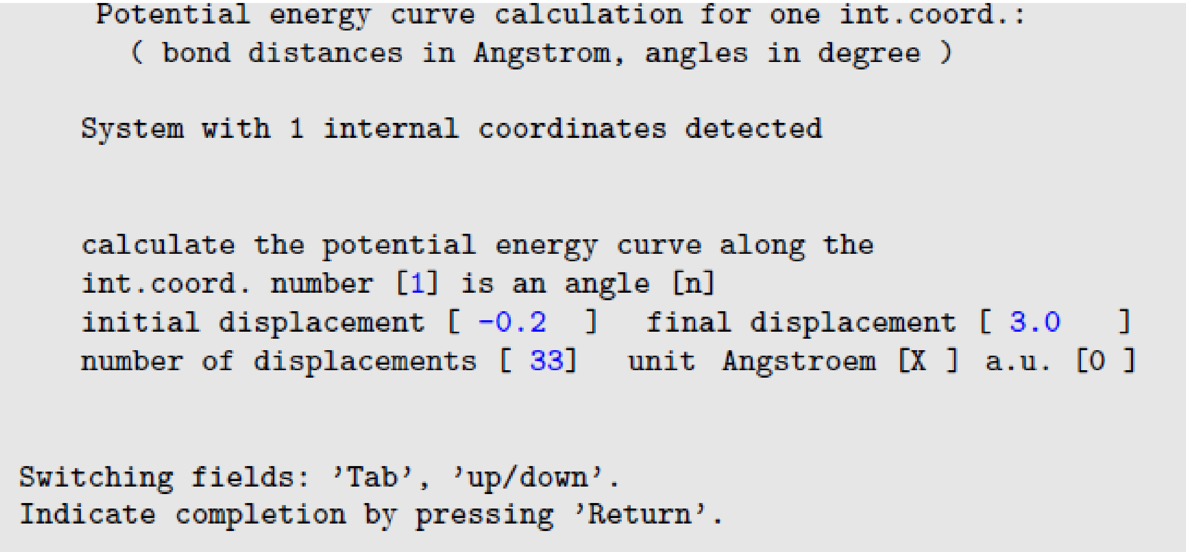
```
                    COLUMBUS INPUT FACILITY

              submenu 1.1.1: single point calculations

 ->  1) (Done with selections)
     2) [ ] SCF
     3) [X] MCSCF
     4) [ ] transition moments for MCSCF
     5) [X] MR-CISD (serial operation)
     6) [ ] MR-CISD (parallel operation)
     7) [ ] SO-CI coupled to non-rel. CI
     8) [ ] one-electron properties for all methods
     9) [X] transition moments for MR-CISD
    10) [ ] single point gradient
    11) [ ] nonadiabatic couplings (and/or gradients)
    12) [ ] <L> value calculation for MR-CISD
    13) [X] convert MOs into molden format
    14) [ ] get starting MOs from a higher symmetry
    15) [ ] finite field calculation for all methods
    16) [ ] include point charges
    17) [ ] extended MOLCAS interface
```



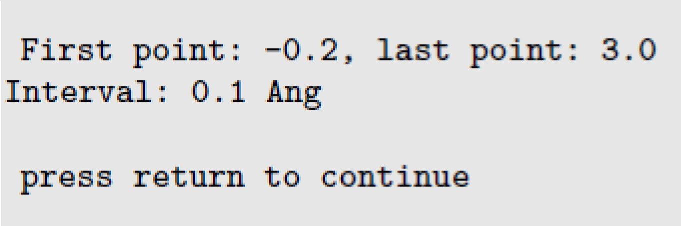
```
                    COLUMBUS INPUT FACILITY

                 submenu 1: type of calculation

     1) Job control for single point or gradient calculation
->   2) Potential energy curve for one int.  coordinate
     3) Vibrational frequencies and force constants
     4) Exit
```



```
Internal coordinates generated
Press return to continue

Internal coordinate file exists, would you like to overwrite it?  (y|n)  y

Internal coordinates generated
Press return to continue
```



```
    Potential energy curve calculation for one int.coord.:
      ( bond distances in Angstrom, angles in degree )

   System with 1 internal coordinates detected


   calculate the potential energy curve along the
   int.coord. number [1] is an angle [n]
   initial displacement [ -0.2  ]   final displacement [ 3.0   ]
   number of displacements [ 33]   unit  Angstroem [X ] a.u. [0 ]


Switching fields: 'Tab', 'up/down'.
Indicate completion by pressing 'Return'.
```



```
 First point: -0.2, last point: 3.0
Interval: 0.1 Ang

 press return to continue
```

Applications : O_2

- All the calculation were created in the DISPLACEMENT folder;

```
ls DISPLACEMENT
```

- First lets run this reference calculation to use it as a first guess;

```
$COLUMBUS/runc -msmp 1000 > runls &
```

- Check the orbitals MOLDEN/ with Jmol.

- The calc.pl script run the calculation for every distance;
- We wish two behaviors from this script:
  - Start the calculation considering the previous converged orbitals as guess;
  - For the first calculation, the guess orbitals are taken from the reference calculation;
- Copy the starting orbitals;

```
cp MOCOEF/mocoef_mc.sp mocoef.start
$COLUMBUS/calc.pl -morestart -m 1000 -nproc 1 >& runsurfls &
```

- The curve.pl script colect the results:

```
$COLUMBUS/curve.pl
```

- We must write the curvein file:

```
msci 1 1
msci 1 2
```

```
$COLUMBUS/curve.pl
```

- Several information are listed:
  - Each calculation convergence status;
  - MRCI and MRCI+Q energies;
  - Take a look at your earliest convenience.

- For the analysis, we need the files in the curve folder:

```
$COLUMBUS/curve.pl > ../curve/curve.out
cp runsurfls ../curve
cd ../curve
```

- There is a script called get_results.py;

```
python3 get_results.py -h
python3 get_results.py -d 33 -c curve.out -r runsurfls
```

Applications : O_2

- The script wrote 3 files:
    - drt1-state1.dat → Potential energy curve for the $^3B_{1g}$ state;
    - drt2-state1.dat → Potential energy curve for the $^3B_{1u}$ state;
    - tm-drt1-state1-drt2-state2.dat → Transition Moment;
    - The x axis are the Columbus displacements;
- The plot is found in **curve.png**.

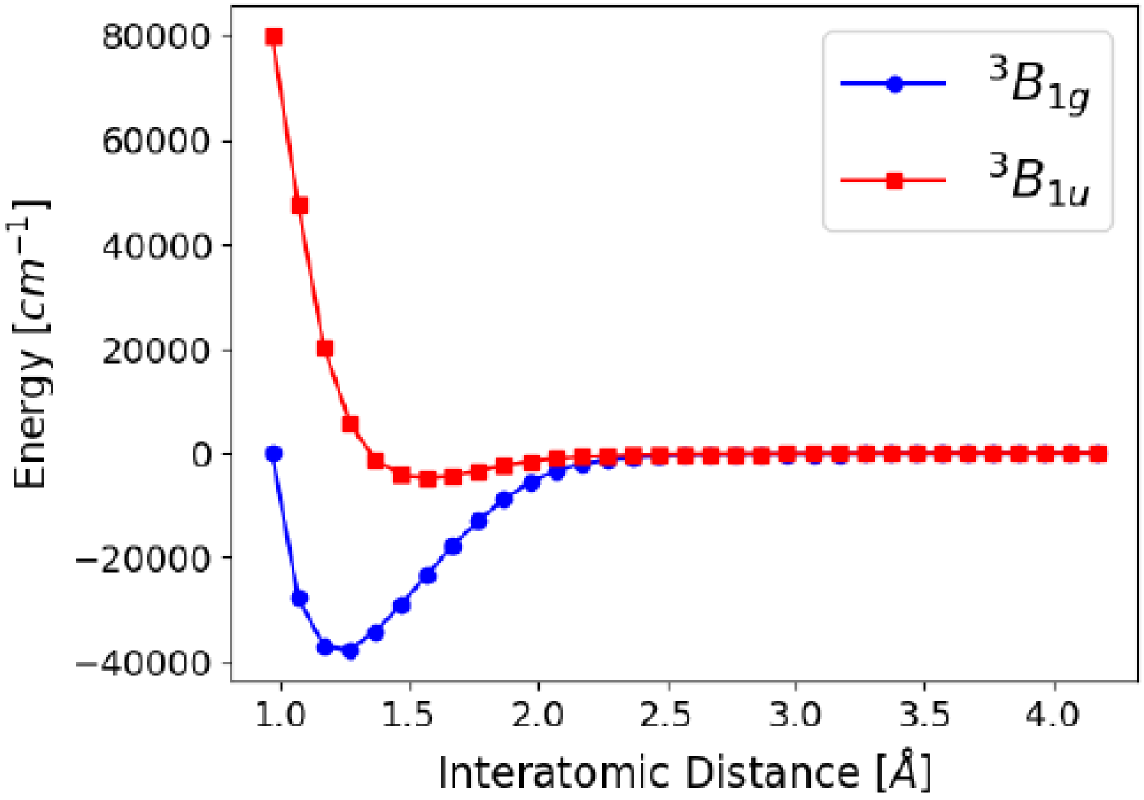
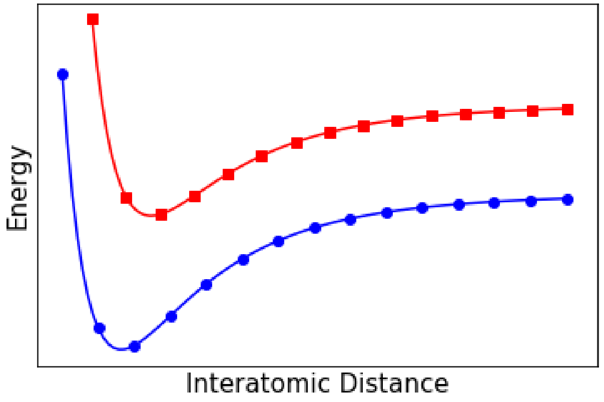
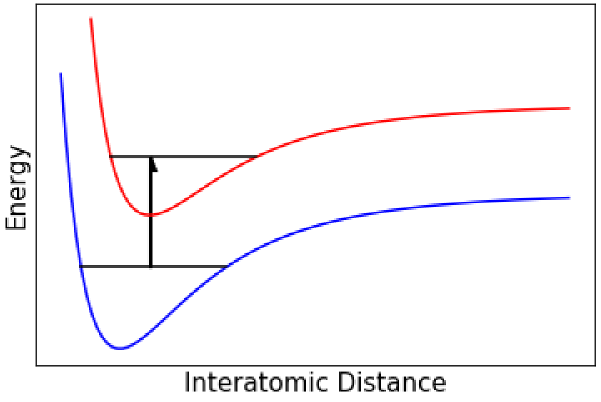


Figure: Expected results for the $^3B_{1g}$ and $^3B_{1u}$ potential energy curves calculated with UMRCI//CAS(12,10)/aug-cc-pVDZ.

Nuclear Equation - DS-ITA

- From Columbus → Solve electronic Schrödinger equation;
- Access Rovibrational spectroscopic information → Solve the Nuclear Hamiltonian;
    - Energy levels;
    - Transition Probabilities;
    - Radiative Lifetimes;

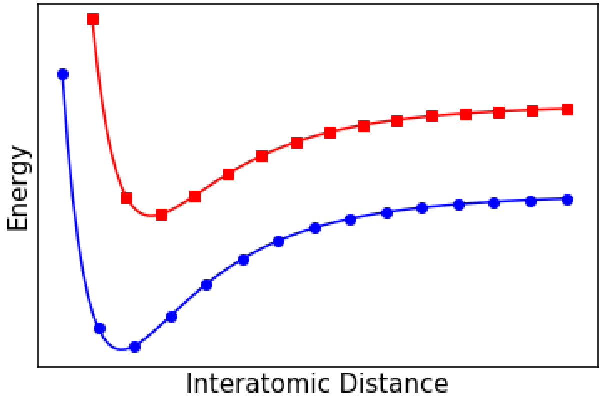


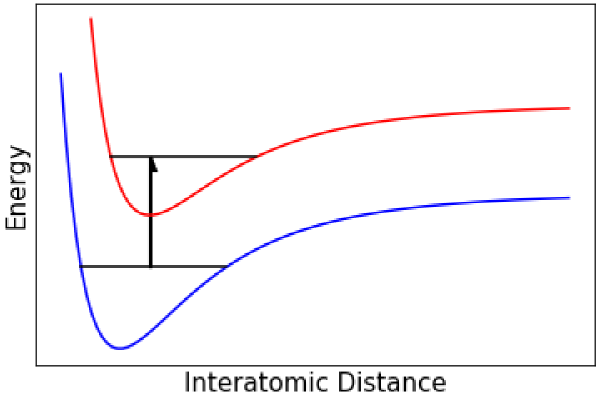


Nuclear Equation - DS-ITA

DS-ITA

- Modern Fortran → Easy to read the code, easy to right input files and easy to read the outputs;
- Calculate a numerical Hamiltonian through the finitte difference method with “arbitrary” order of approximation;
- Only the desired eigenvalues are calculated;

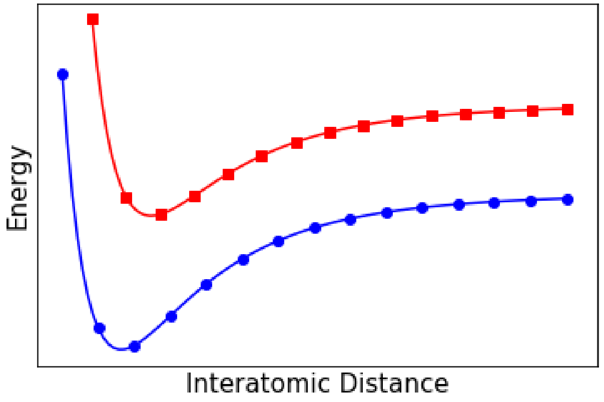


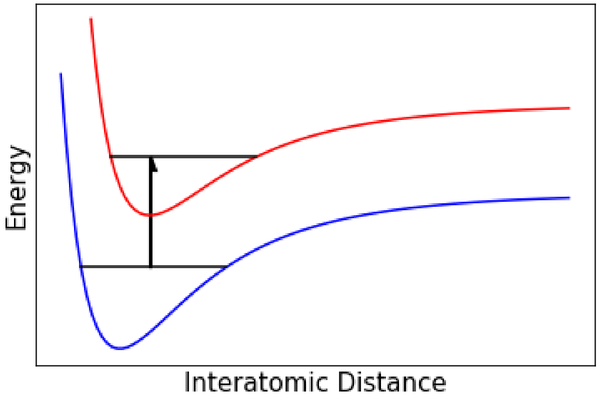


Nuclear Equation - DS-ITA

DS-ITA

- The solution trustworth does not deppend on the quality of the potential fit;
- Since the eigenvalues are calculated, there is no need for a first guess (Numerov like methods);
- The code can be linked against OpenBlas and use OpenMP parallelization.





Nuclear Equation - DS-ITA

DS-ITA

- Available from February for alpha test;
- Contact the developer → Rene F. K. Spada <rfkspada@ita.com>
- Thanks.