Lecture B8
Molecular Orbital Theory, Part 3

Moving to the Suburbs

Molecular Orbital Theory - LCAO-MO

Robert S. Mulliken realized that a Linear Combination of Atomic Orbitals (LCAO) could be used to make a set of new Molecular Orbitals (MO). The energies of these new molecular orbitals could be calculated and then filled with valence electrons.

Robert S. Mulliken
1896-1986

Mulliken received the 1966 Nobel Prize for his work.

MO energies come from Quantum Mechanics, of course!

$$\hat{H}\left|\Psi_n\right\rangle = E_n\left|\Psi_n\right\rangle$$

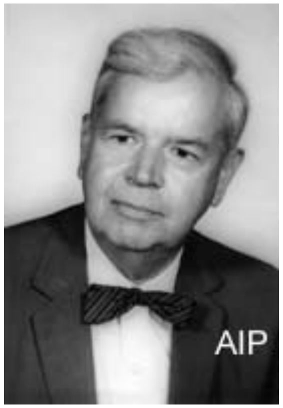
WHEN we solve the Schrödinger equation, we always obtain two things:

1. a set of eigenstates.
2. a set of eigenstate energies.

If you are interested, please look up the "Hartree-Fock Method" and "Slater Determinants."

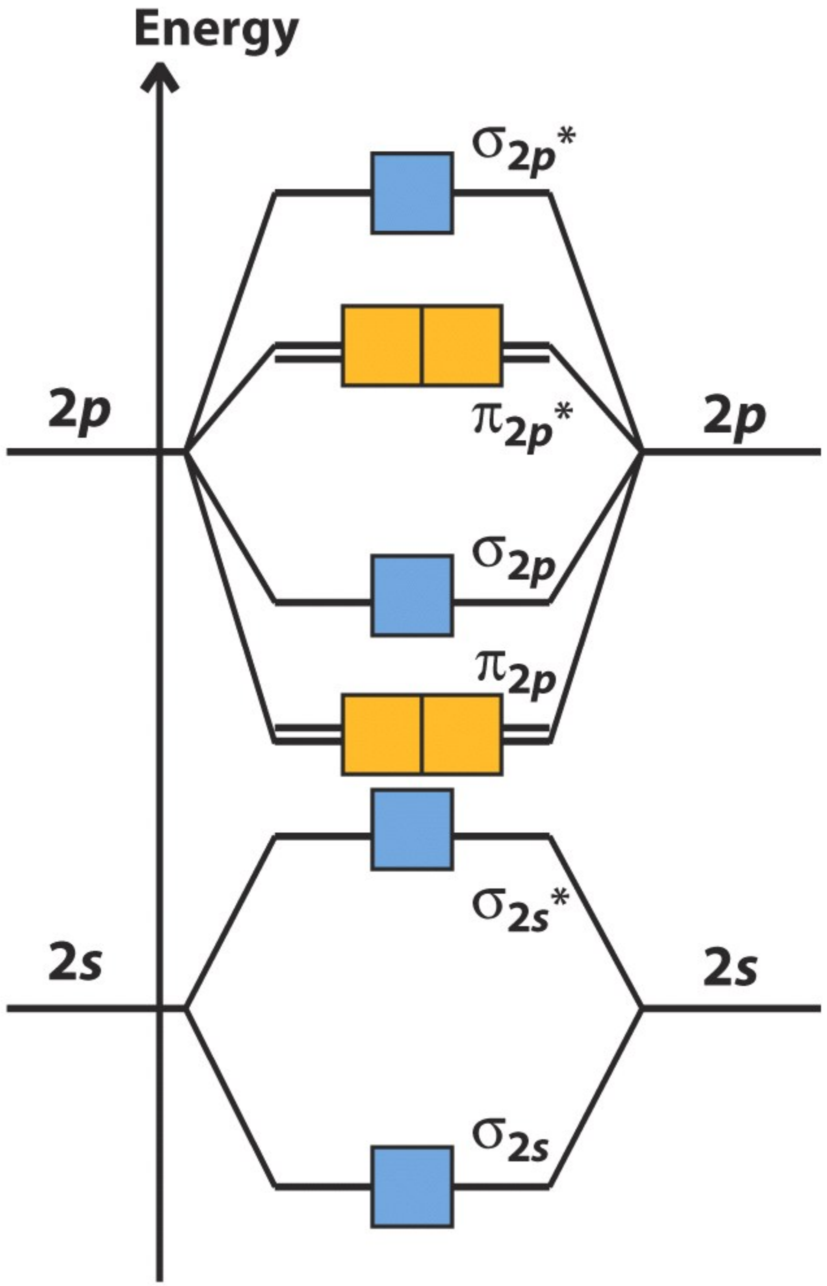
D. R. Hartree
1897-1958

V. A. Fock
1898-1974



J. C. Slater
1900-1976

A final homonuclear example: C_2 - Number of valence electrons?



For homonuclear diatomic molecules, you should be able to predict:

I. Electron Configuration

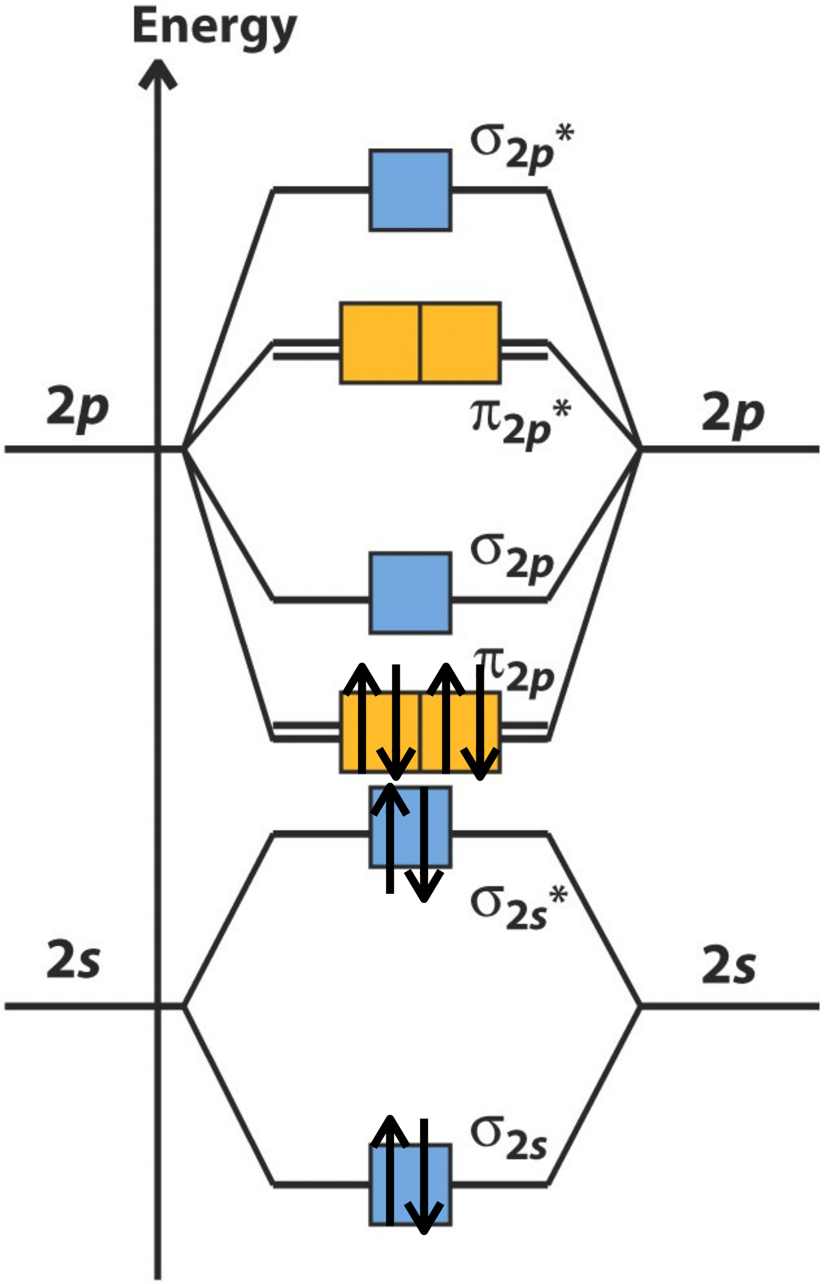
II. Bond Order

III. Paramagnetic or Diamagnetic

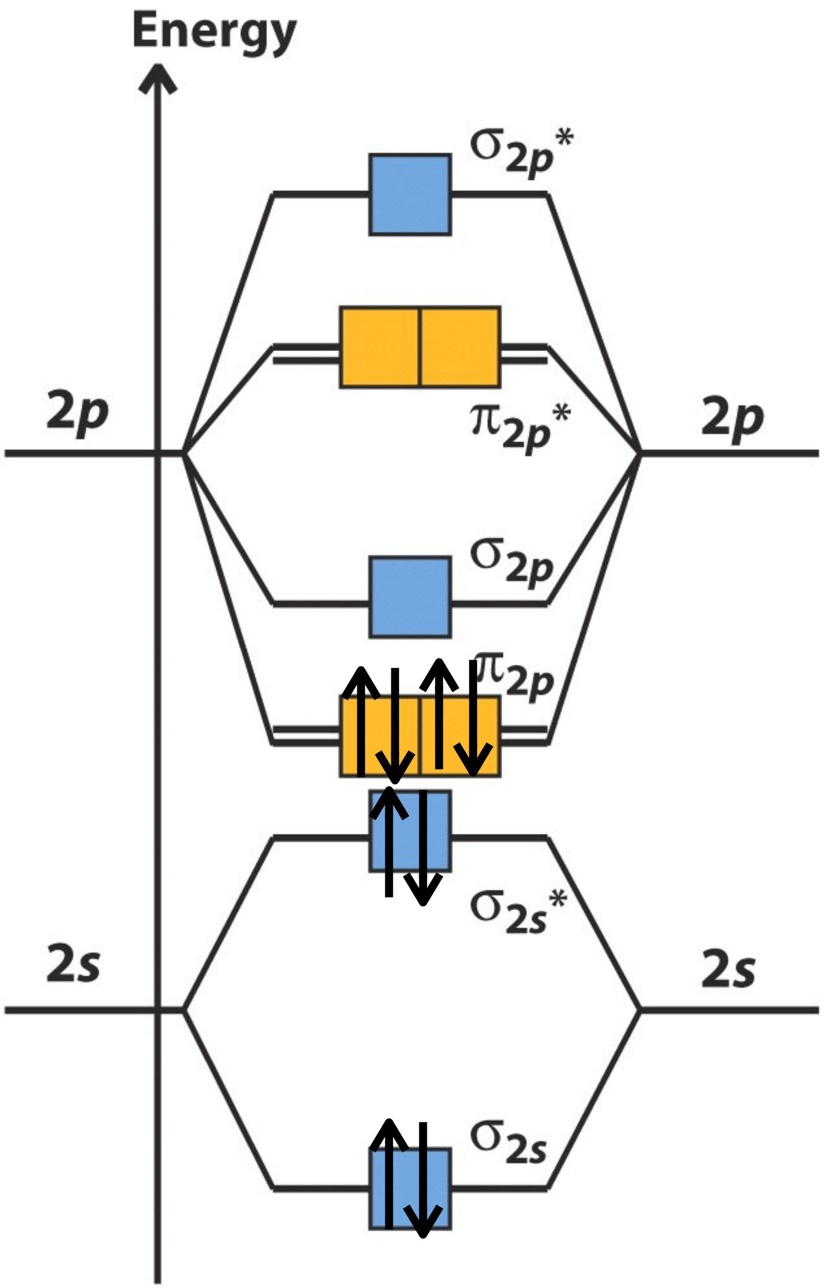
IV. Number of electrons in the HOMO

V. Estimate (set limits on) the IP of the molecule

A final homonuclear example: C_2 - 8 electrons
- state ordering same as N_2



A final example: C_2 - 8 electrons - state ordering same as N_2



We predict:

bond order = 1/2(6-2) = 2

C_2 is diamagnetic

IP is greater than 11.26 eV

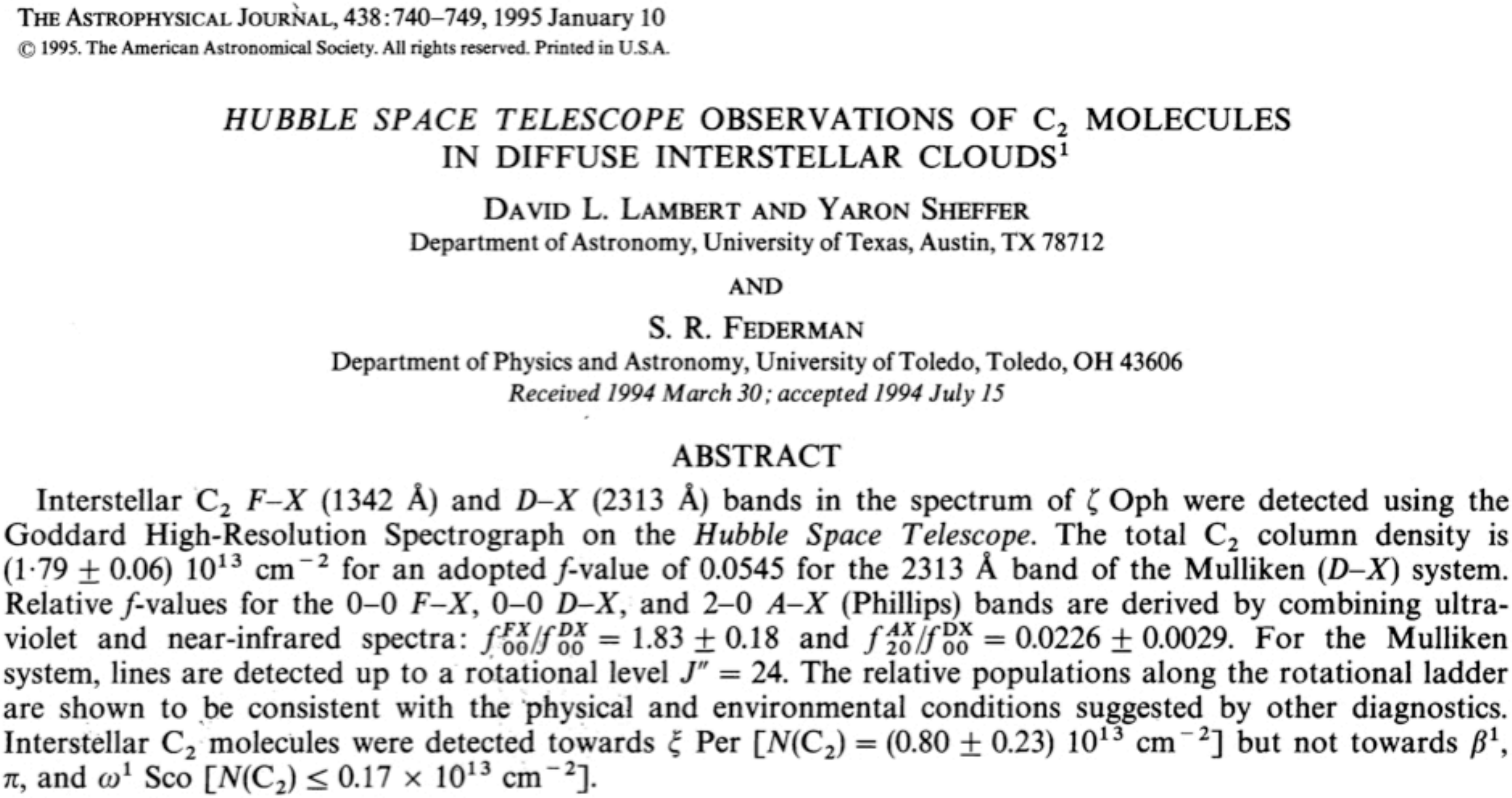
electron configuration is:

$\sigma_{2s}^2\,\sigma^*{}_{2s}^2\,\pi_{2p}^4$

Four electrons in the HOMO

By the way, does C_2 exist?

By the way, does C_2 exist?



THE ASTROPHYSICAL JOURNAL, 438:740–749, 1995 January 10

HUBBLE SPACE TELESCOPE OBSERVATIONS OF C_2 MOLECULES IN DIFFUSE INTERSTELLAR CLOUDS[1]

DAVID L. LAMBERT AND YARON SHEFFER
Department of Astronomy, University of Texas, Austin, TX 78712

AND

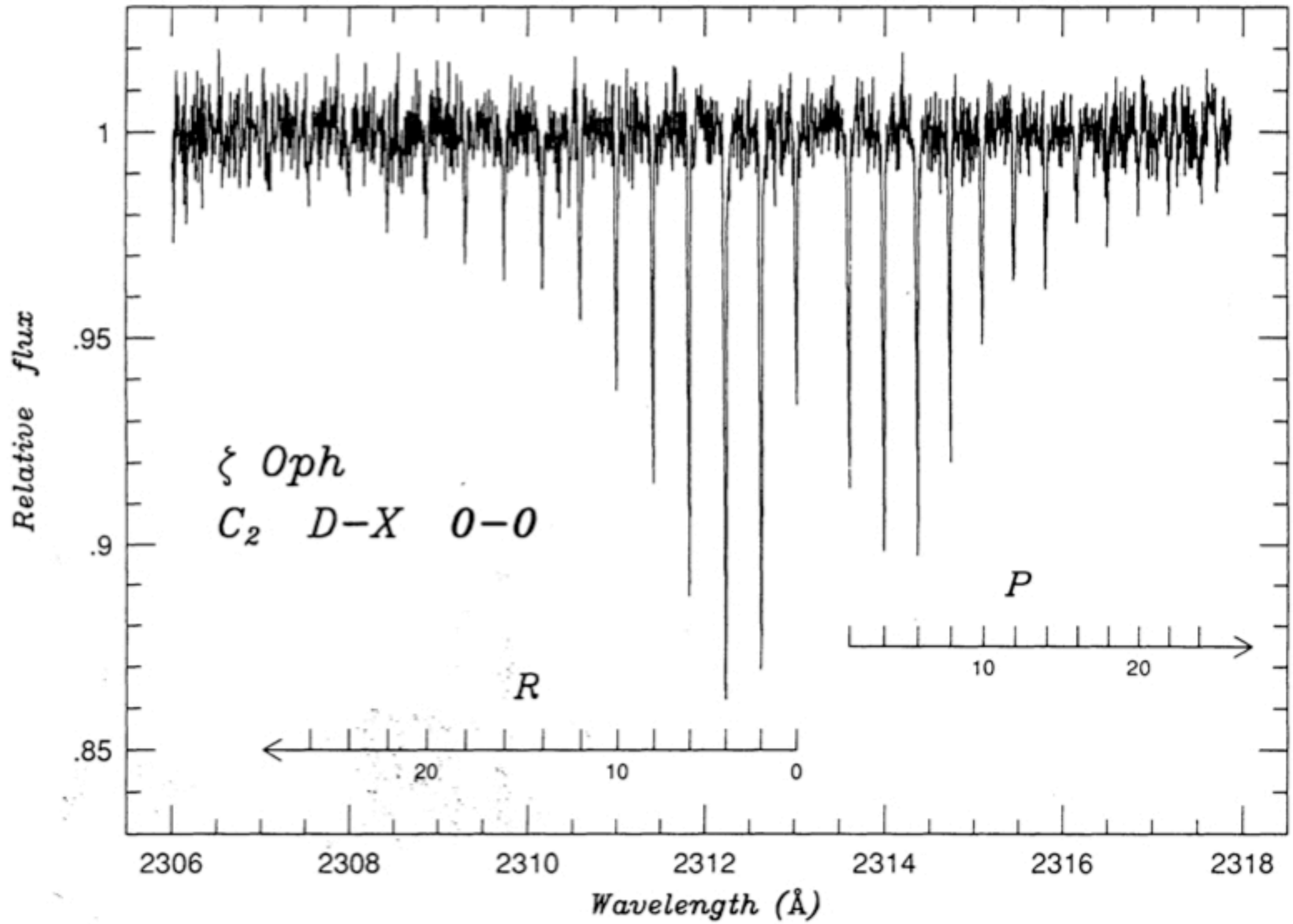
S. R. FEDERMAN
Department of Physics and Astronomy, University of Toledo, Toledo, OH 43606
Received 1994 March 30; accepted 1994 July 15

ABSTRACT

Interstellar C_2 F–X (1342 Å) and D–X (2313 Å) bands in the spectrum of ζ Oph were detected using the Goddard High-Resolution Spectrograph on the *Hubble Space Telescope*. The total C_2 column density is $(1{\cdot}79 \pm 0.06)\ 10^{13}\ \mathrm{cm}^{-2}$ for an adopted f-value of 0.0545 for the 2313 Å band of the Mulliken (D–X) system. Relative f-values for the 0–0 F–X, 0–0 D–X, and 2–0 A–X (Phillips) bands are derived by combining ultraviolet and near-infrared spectra: $f^{FX}_{00}/f^{DX}_{00} = 1.83 \pm 0.18$ and $f^{AX}_{20}/f^{DX}_{00} = 0.0226 \pm 0.0029$. For the Mulliken system, lines are detected up to a rotational level $J'' = 24$. The relative populations along the rotational ladder are shown to be consistent with the physical and environmental conditions suggested by other diagnostics. Interstellar C_2 molecules were detected towards ξ Per $[N(C_2) = (0.80 \pm 0.23)\ 10^{13}\ \mathrm{cm}^{-2}]$ but not towards β^1, π, and ω^1 Sco $[N(C_2) \leq 0.17 \times 10^{13}\ \mathrm{cm}^{-2}]$.

Yes it does -- in outer space!

Here's some of the "Mulliken bands" of interstellar C_2

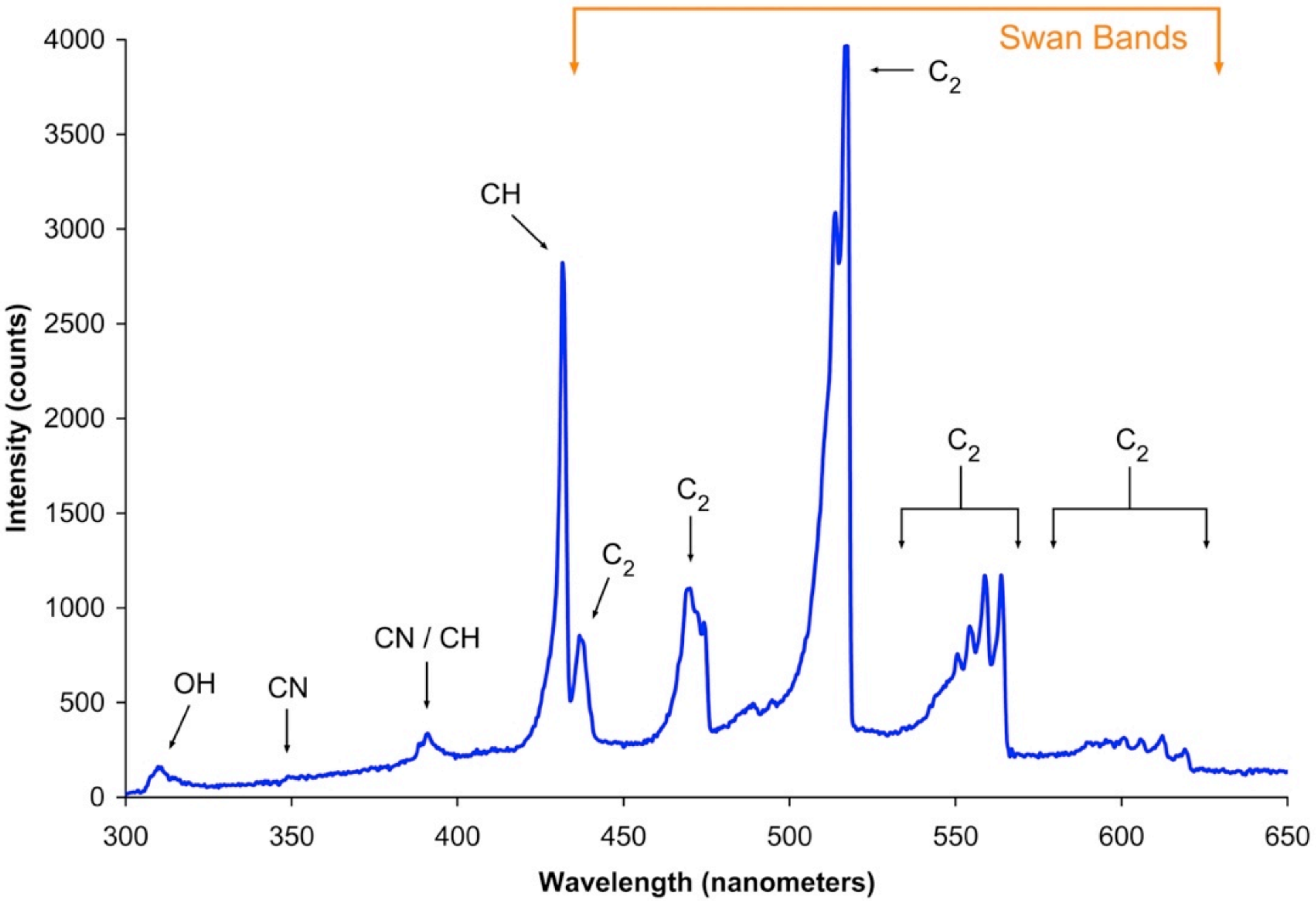


But C_2 also exists inside your bunsen burner:

Swan bands are a characteristic of the spectra of carbon stars, comets and of burning hydrocarbon fuels. They are named for the Scottish physicist William Swan who first studied the spectral analysis of carbon C_2 in 1856.

Identified as C_2 by J. D. Shea in 1927:
Phys. Rev. 30 (1927) 825–843.

The Swan bands are the blue emission lines in a Bunsen burner.



Spectrum of a blue flame from a pocket butane torch clearly showing non-continuum spectral emission. Spectrum taken by me using an Ocean Optics HR2000 spectrometer.

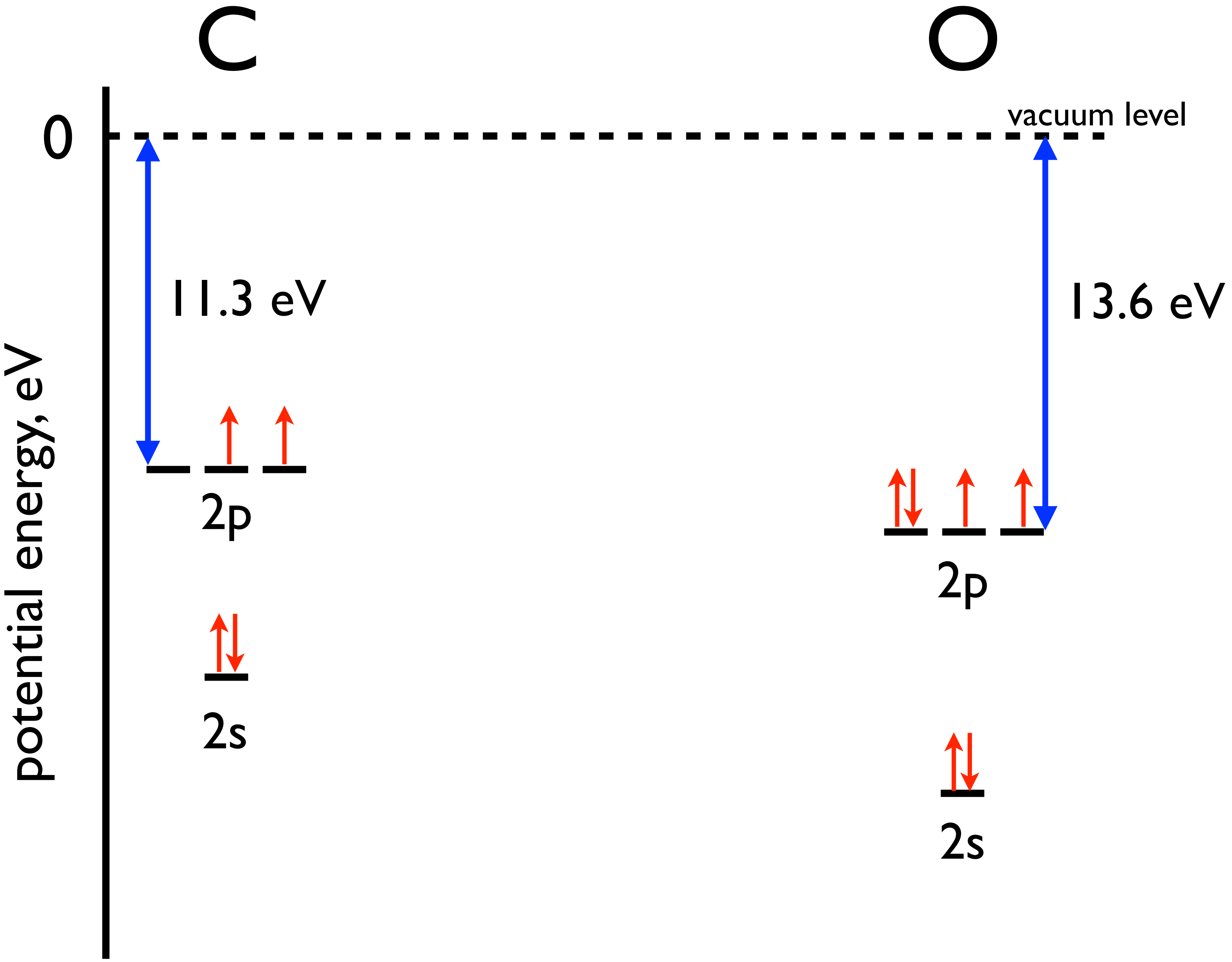
Heteronuclear Diatomics

The fool-proof procedure for constructing energy correlation diagrams for heteronuclear diatomics:

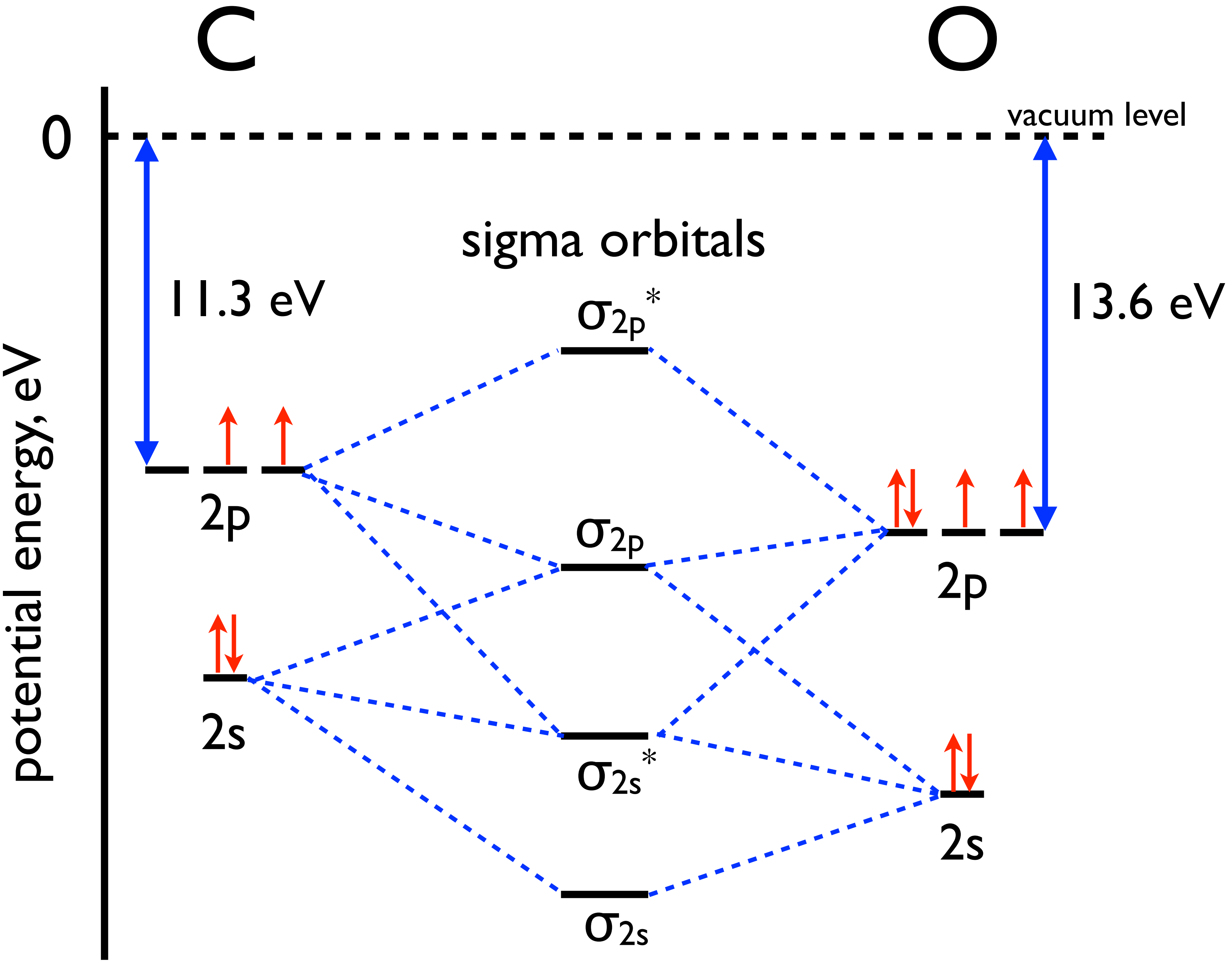
0. Draw the vacuum level.
1. Put the atomic orbitals for each bonding partner in your diagram. *Position the HOAO based upon the IP of the atom.*
2. Draw in the energy levels for your MOs. *You'll need one for each atomic state.*
3. Fill them with electrons. *Make sure to follow Aufbau and Hund's rules.*

Easy as Toast!

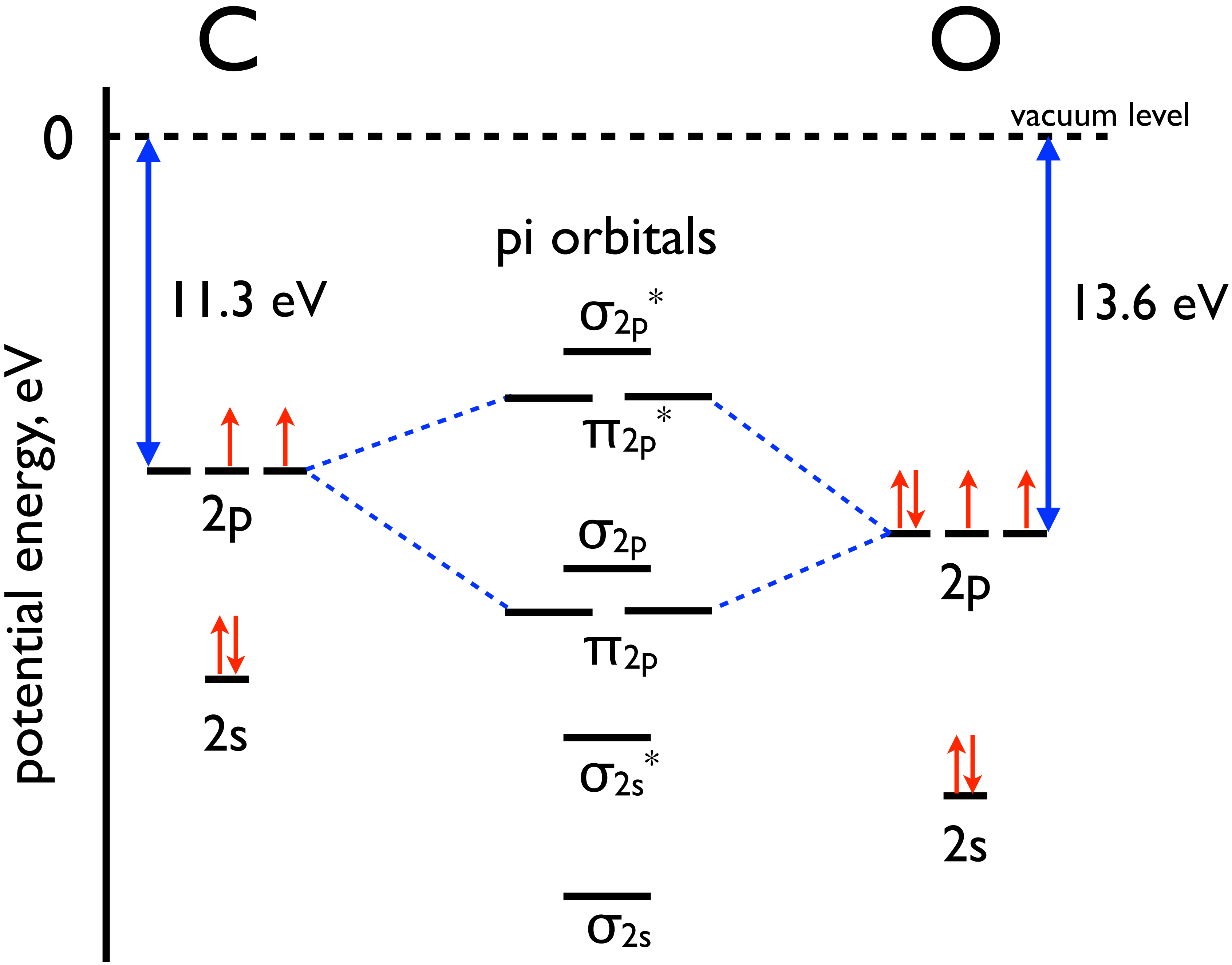
A example: Carbon Monoxide (CO)



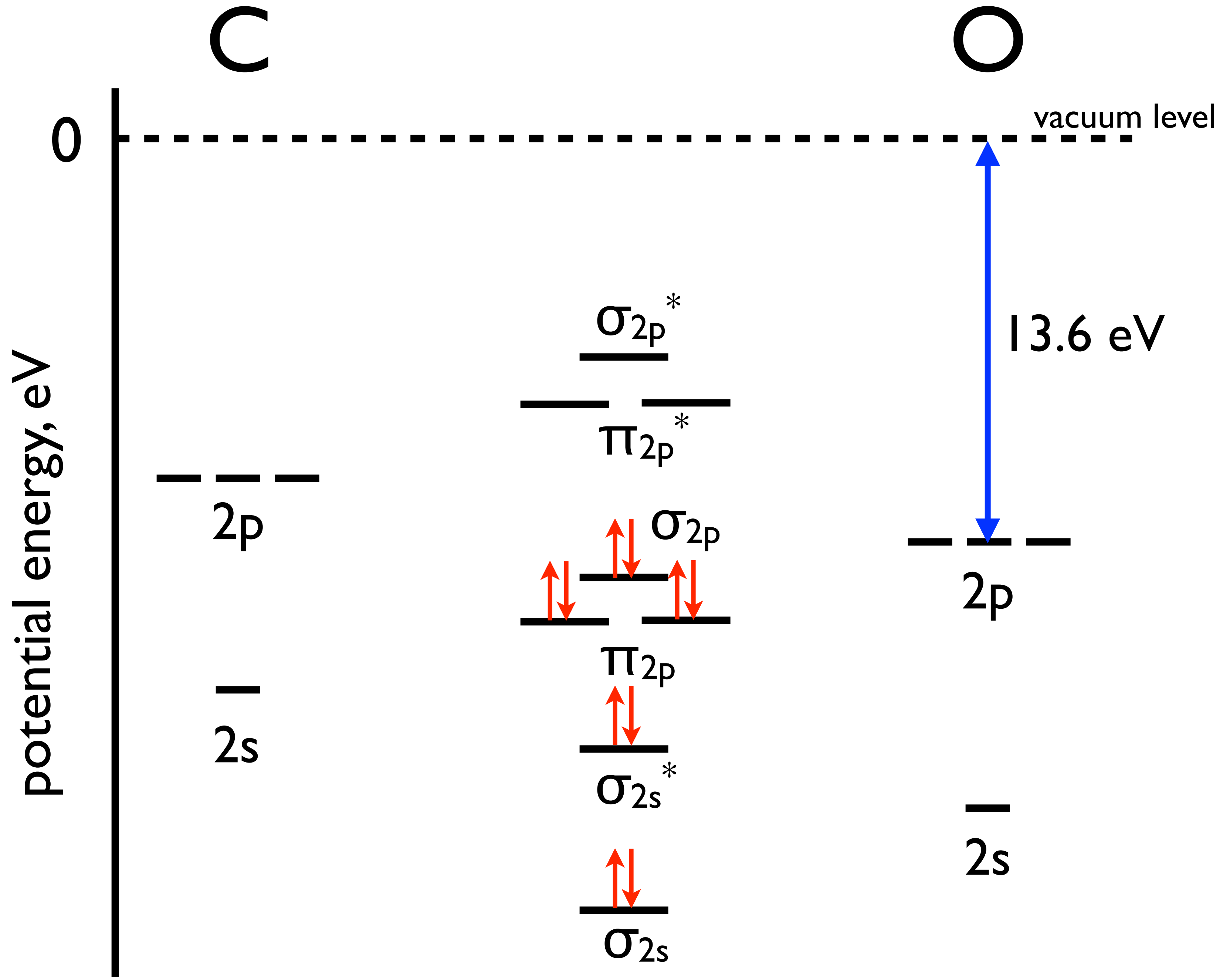
An example: Carbon Monoxide (CO)



An example: Carbon Monoxide (CO)



An example: Carbon Monoxide (CO) - 10 valence electrons



So heteronuclear diatomic molecules are a bit more complicated, but still we can make predictions:

For CO:

bond order = **3.0**

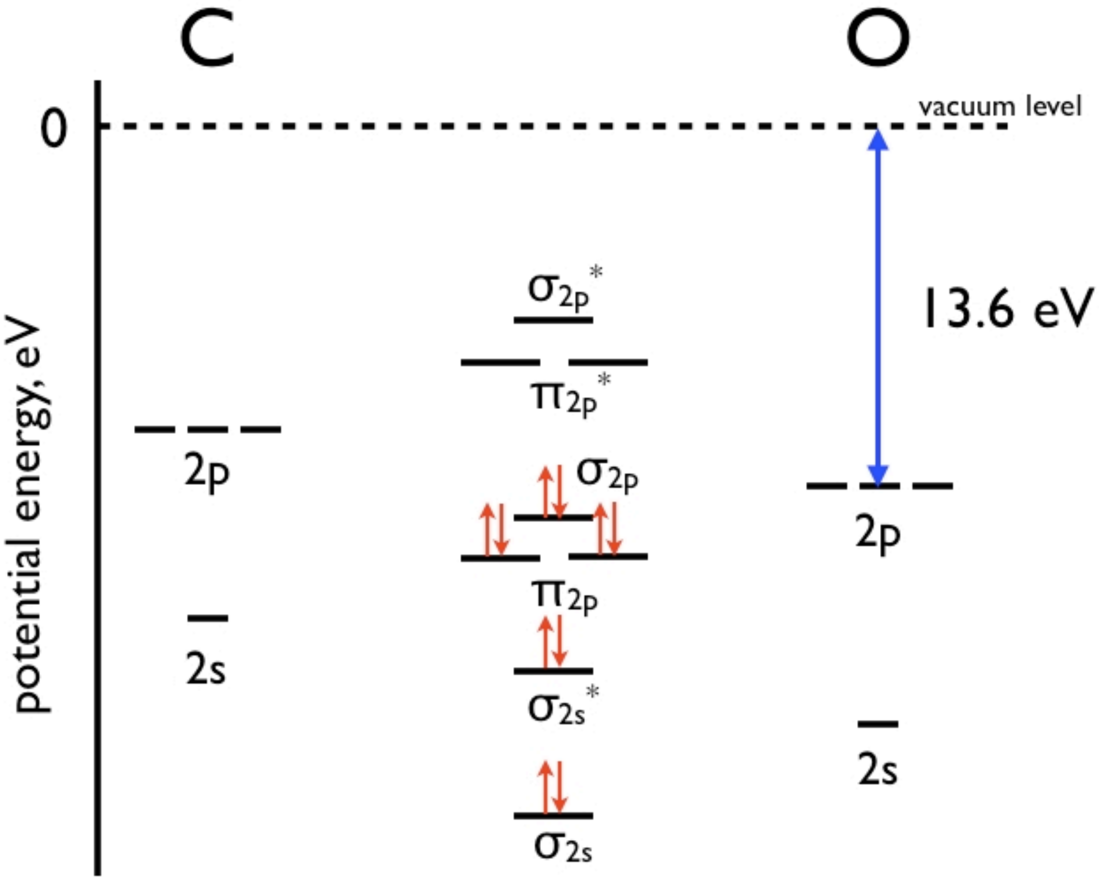
CO is **diamagnetic**

IP is greater than 13.6 eV
(Actual is 14.0 eV)

Electron configuration is:

$\sigma_{2s}{}^2\ \sigma^*{}_{2s}{}^2\ \pi_{2p}{}^4\sigma_{2p}{}^2$

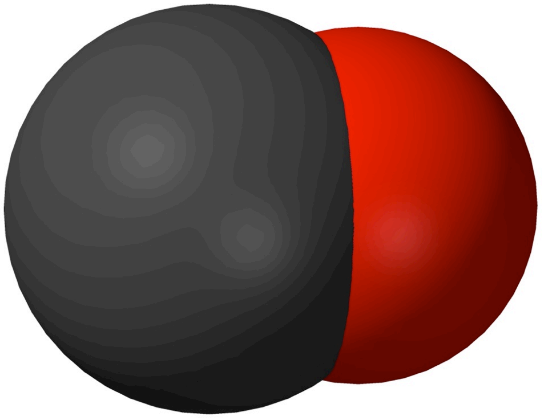
Two electrons in the HOMO

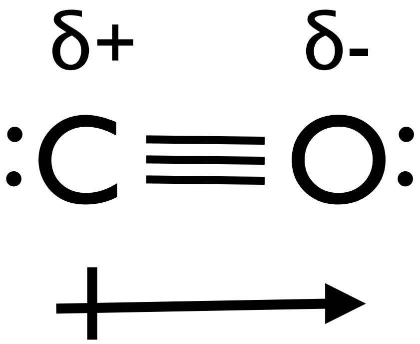


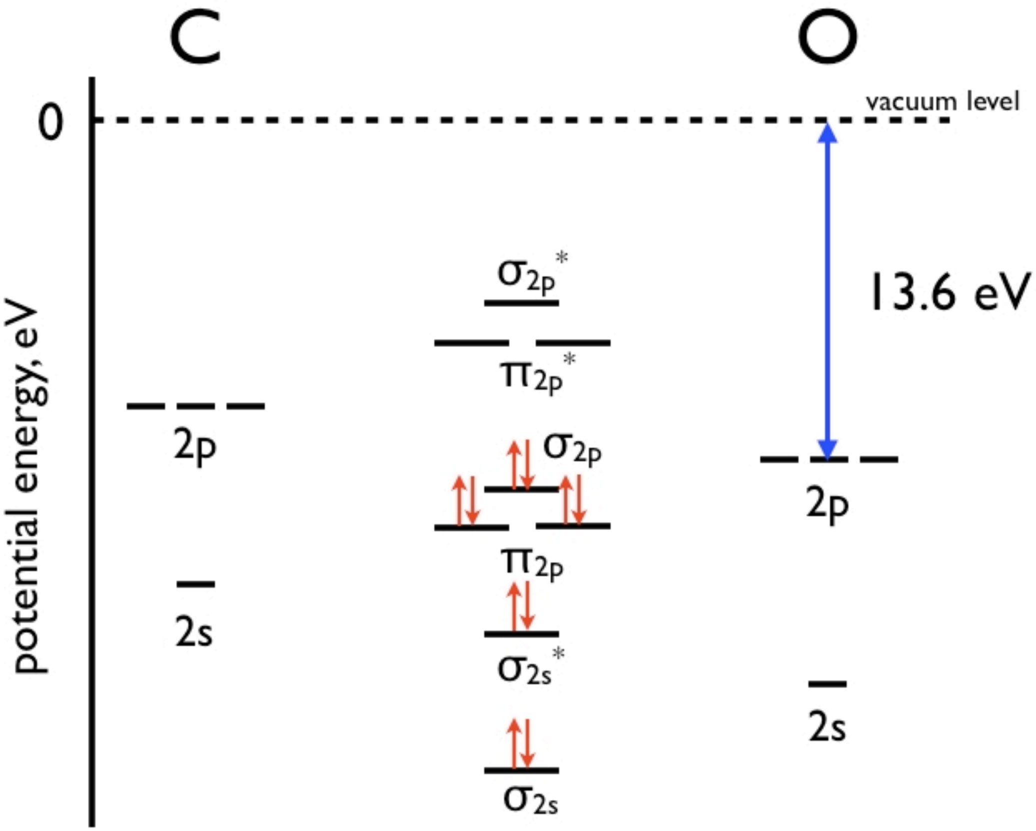
Some additional facts about CO:

Bond Length: 112.8 pm

Dipole Moment: 0.112D

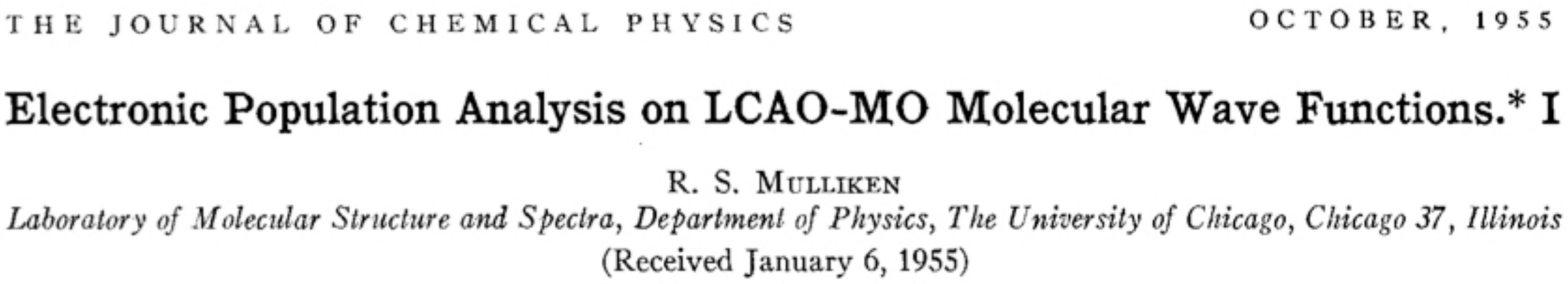






Opposite of Lewis Dot Structure Formal Charge!

Mulliken Population Analysis



THE JOURNAL OF CHEMICAL PHYSICS OCTOBER, 1955

Electronic Population Analysis on LCAO-MO Molecular Wave Functions.* I

R. S. MULLIKEN

Laboratory of Molecular Structure and Spectra, Department of Physics, The University of Chicago, Chicago 37, Illinois

(Received January 6, 1955)

Mulliken outlined a systematic method for obtaining quantitative information from the LCAO-MOs in terms of atomic populations (net and gross), overlap populations, promotion and the total charge on each atom.

In 1955.

Robert S. Mulliken
1896-1986

Mulliken Population Analysis

For a diatomic molecule AB, consider a molecular orbital ϕ_{MO} that is made from a linear combination of two atomic orbitals, one from atom A, and one from atom B.

$$\phi_{MO} = c_A \psi_A + c_B \psi_B$$

Mulliken Population Analysis

For a diatomic molecule AB, consider a molecular orbital ϕ_{MO} that is made from a linear combination of two atomic orbitals, one from atom A, and one from atom B.

$$\phi_{MO} = c_A \psi_A + c_B \psi_B$$

The molecular orbital and both of the atomic orbitals are all normalized to a probability of one over all space:

$$\int \phi_{MO}^2 d\tau = 1 \quad \int \psi_A^2 d\tau = 1 \quad \int \psi_B^2 d\tau = 1$$

Mulliken Population Analysis

The Born Interpretation states that Φ^2 is the probability density for the molecular orbital:

$$\phi_{MO}^2 = c_A^2\psi_A^2 + 2c_A c_B \psi_A \psi_B + c_B^2\psi_B^2$$

Mulliken Population Analysis

The Born Interpretation states that Φ^2 is the probability density for the molecular orbital:

$$\phi_{MO}^2 = c_A^2\psi_A^2 + 2c_A c_B \psi_A \psi_B + c_B^2 \psi_B^2$$

If we integrate this equation to get the probability, we end up with three terms:

$$\int \phi_{MO}^2 d\tau = c_A^2 \int \psi_A^2 d\tau + 2c_A c_B \int \psi_A \psi_B d\tau + c_B^2 \int \psi_B^2 d\tau$$

Mulliken Population Analysis

If we integrate this equation to get the probability, we end up with three terms:

$$\overset{\text{one}}{\boxed{\int \phi_{MO}^2 d\tau}} = c_A^2 \overset{\text{one}}{\boxed{\int \psi_A^2 d\tau}} + 2c_A c_B \boxed{\int \psi_A \psi_B d\tau} + c_B^2 \overset{\text{one}}{\boxed{\int \psi_B^2 d\tau}}$$

$$\boxed{1 = c_A^2 + 2c_A c_B S_{AB} + c_B^2}$$

where S_{AB} is called the overlap integral:

$$S_{AB} = \int \psi_A \psi_B d\tau$$

Mulliken Population Analysis

If there are N electrons in the molecular orbital Φ, then:

$$N = Nc_A^2 + 2Nc_A c_B S_{AB} + Nc_B^2$$

Mulliken Population Analysis

If there are N electrons in the molecular orbital Φ, then:

$$N = \boxed{Nc_A^2} + 2Nc_Ac_BS_{AB} + \boxed{Nc_B^2}$$

Mulliken called Nc_A^2 the net atomic population on atom A and Nc_B^2 the net atomic population on atom B.

Mulliken Population Analysis

If there are N electrons in the molecular orbital Φ, then:

$$N = Nc_A^2 + \boxed{2Nc_A c_B S_{AB}} + Nc_B^2$$

Mulliken called Nc_A^2 the net atomic population on atom A and Nc_B^2 the net atomic population on atom B.

Mulliken called $2Nc_Ac_BS_{AB}$ the overlap population, and used it as a measure of the amount of bonding in the orbital.

Mulliken Population Analysis

If there are N electrons in the molecular orbital Φ, then:

$$\boxed{N = Nc_A^2 + 2Nc_A c_B S_{AB} + Nc_B^2}$$

Mulliken called Nc_A^2 the net atomic population on atom A and Nc_B^2 the net atomic population on atom B.

Mulliken called $2Nc_A c_B S_{AB}$ the overlap population, and used it as a measure of the amount of bonding in the orbital.

"These three sub-populations may be likened to those of two cities and a (joint) suburb which lies between them."

R. S. Mulliken

Mulliken Population Analysis

Gross Atomic Populations:

Mulliken also created gross atomic populations in which the charge in an orbital was assigned to either atom A or atom B. The overlap population was equally divided between the two atoms.

$$N = Nc_A^2 + 2Nc_Ac_BS_{AB} + Nc_B^2$$

$$N = \underset{N(A)}{\boxed{Nc_A^2 + Nc_Ac_BS_{AB}}} + \underset{N(B)}{\boxed{Nc_Ac_BS_{AB} + Nc_B^2}}$$

$$N = N(A) + N(B)$$

Mulliken Population Analysis

Gross Atomic Populations:

$$N = N(A) + N(B)$$

Gross Atomic Charges:

Mulliken also created gross atomic charges by subtracting the gross atomic populations from the number of electrons originally in the atomic orbitals: $N_0(A)$ and $N_0(B)$.

$$Q(A) = N_0(A) - N(A)$$

$$Q(B) = N_0(B) - N(B)$$

Mulliken Population Analysis

All of the equations I have used were for one MO:

$$\phi_{MO} = c_A\psi_A + c_B\psi_B$$

$$N = Nc_A^2 + 2Nc_Ac_BS_{AB} + Nc_B^2$$

$$N = N(A) + N(B)$$

Mulliken generalized these equations to ALL of the MOs in a molecule. See the Handouts Section of the Chem H2A web page to download his 1955 paper.

R. S. Mulliken, J. Chem. Phys. **10** 1833-1840 (1955).

Mulliken did an example molecule: Carbon Monoxide!

He used the LCAO-MOs from someone else (Sahni):

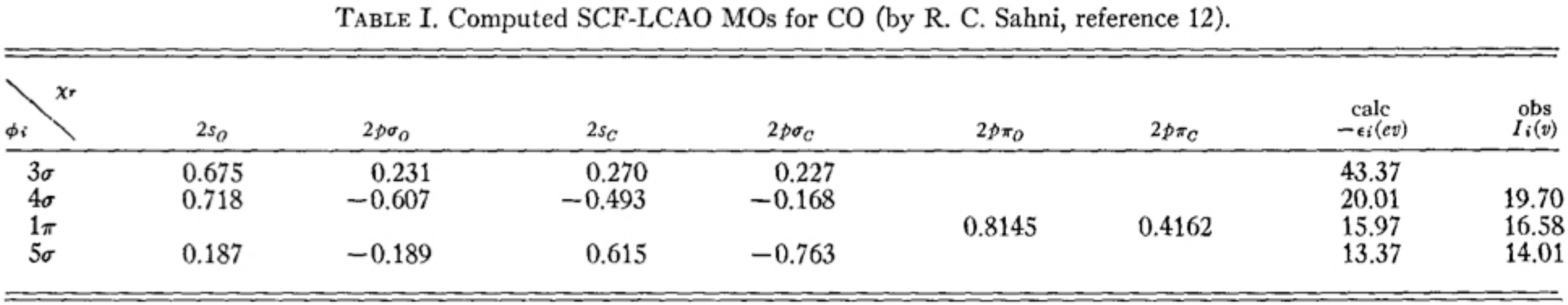


TABLE I. Computed SCF-LCAO MOs for CO (by R. C. Sahni, reference 12).

ϕ_i \ χ_r	$2s_O$	$2p\sigma_O$	$2s_C$	$2p\sigma_C$	$2p\pi_O$	$2p\pi_C$	calc $-\epsilon_i(ev)$	obs $I_i(v)$
3σ	0.675	0.231	0.270	0.227			43.37	
4σ	0.718	−0.607	−0.493	−0.168			20.01	19.70
1π					0.8145	0.4162	15.97	16.58
5σ	0.187	−0.189	0.615	−0.763			13.37	14.01

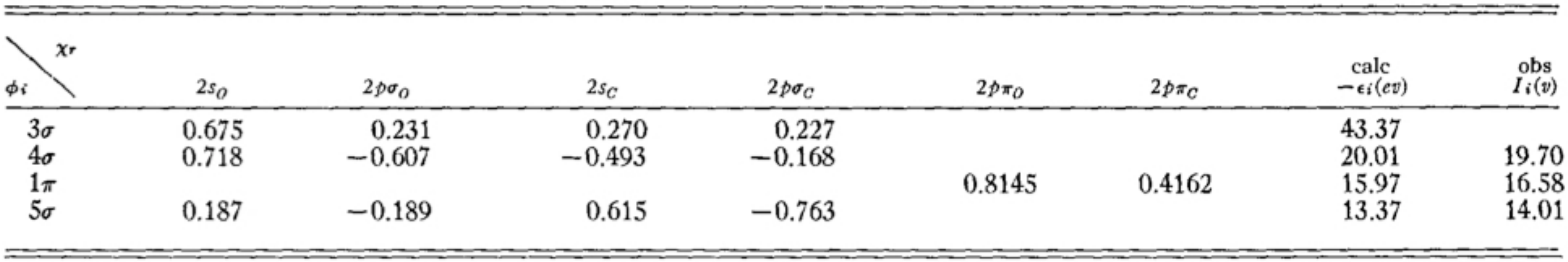
Nomenclature: Mulliken just named the orbitals nσ or nπ:

Ours: $\sigma_{1s}^2\ \sigma^*_{1s}{}^2\ \sigma_{2s}^2\ \sigma^*_{2s}{}^2\ \pi_{2p}^4\sigma_{2p}^2$

His: $1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 4\sigma^2\ 1\pi^2\ 5\sigma^2$

Mulliken did an example molecule: Carbon Monoxide!

TABLE I. Computed SCF-LCAO MOs for CO (by R. C. Sahni, reference 12).



χ_r / ϕ_i	$2s_O$	$2p\sigma_O$	$2s_C$	$2p\sigma_C$	$2p\pi_O$	$2p\pi_C$	calc $-\epsilon_i(ev)$	obs $I_i(v)$
3σ	0.675	0.231	0.270	0.227			43.37	
4σ	0.718	−0.607	−0.493	−0.168			20.01	19.70
1π					0.8145	0.4162	15.97	16.58
5σ	0.187	−0.189	0.615	−0.763			13.37	14.01

Here are the highest energy occupied MOs:

$$5\sigma = 0.187\Psi_O(2s) - 0.189\Psi_O(2p\sigma) + 0.615\Psi_C(2s) - 0.763\Psi_C(2p\sigma)$$

$$1\pi = 0.8145\Psi_O(2p\pi) + 0.4162\Psi_C(2p\pi)$$

The sigma orbitals are all linear combinations
of four orbitals; the pi orbitals of two.

An example: CO

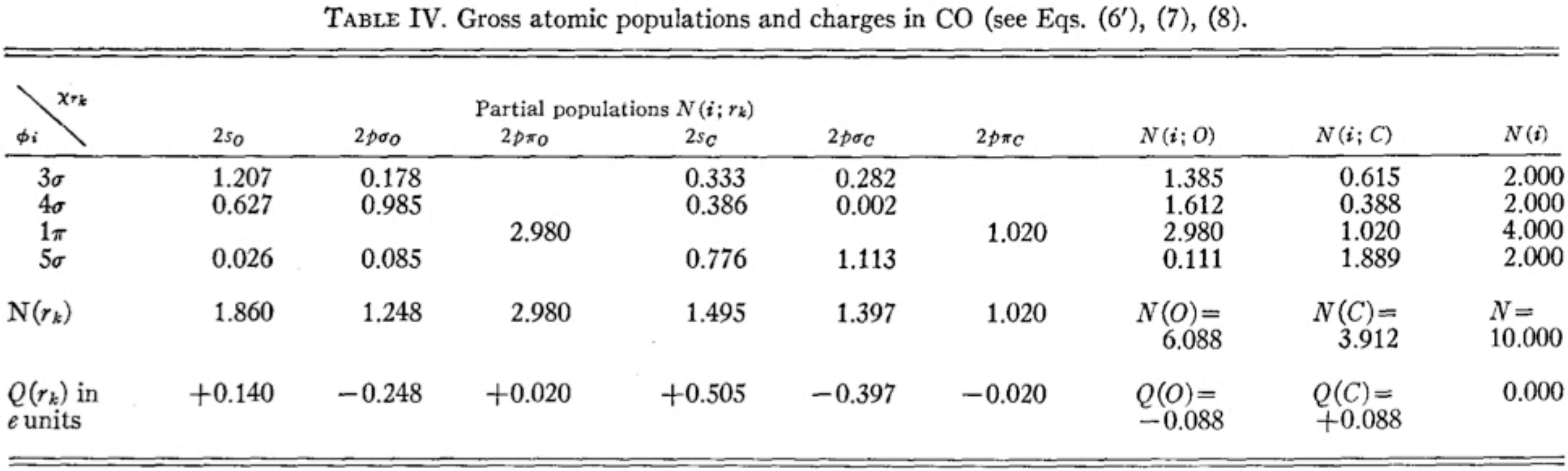


TABLE IV. Gross atomic populations and charges in CO (see Eqs. (6′), (7), (8).

$\phi_i \backslash \chi_{r_k}$	Partial populations $N(i; r_k)$ $2s_O$	$2p\sigma_O$	$2p\pi_O$	$2s_C$	$2p\sigma_C$	$2p\pi_C$	$N(i; O)$	$N(i; C)$	$N(i)$
3σ	1.207	0.178		0.333	0.282		1.385	0.615	2.000
4σ	0.627	0.985		0.386	0.002		1.612	0.388	2.000
1π			2.980			1.020	2.980	1.020	4.000
5σ	0.026	0.085		0.776	1.113		0.111	1.889	2.000
$N(r_k)$	1.860	1.248	2.980	1.495	1.397	1.020	$N(O)=$ 6.088	$N(C)=$ 3.912	$N=$ 10.000
$Q(r_k)$ in e units	+0.140	−0.248	+0.020	+0.505	−0.397	−0.020	$Q(O)=$ −0.088	$Q(C)=$ +0.088	0.000

Using the atomic populations, we find:

On the Carbon($1s^2 2s^2 2p^2$): $1s^{2.00} 2s^{1.49} 2p^{2.42}$

On the Oxygen($1s^2 2s^2 2p^4$): $1s^{2.00} 2s^{1.86} 2p^{4.23}$

Pauling was right: sp promotion and hybridization exists!

An example: CO

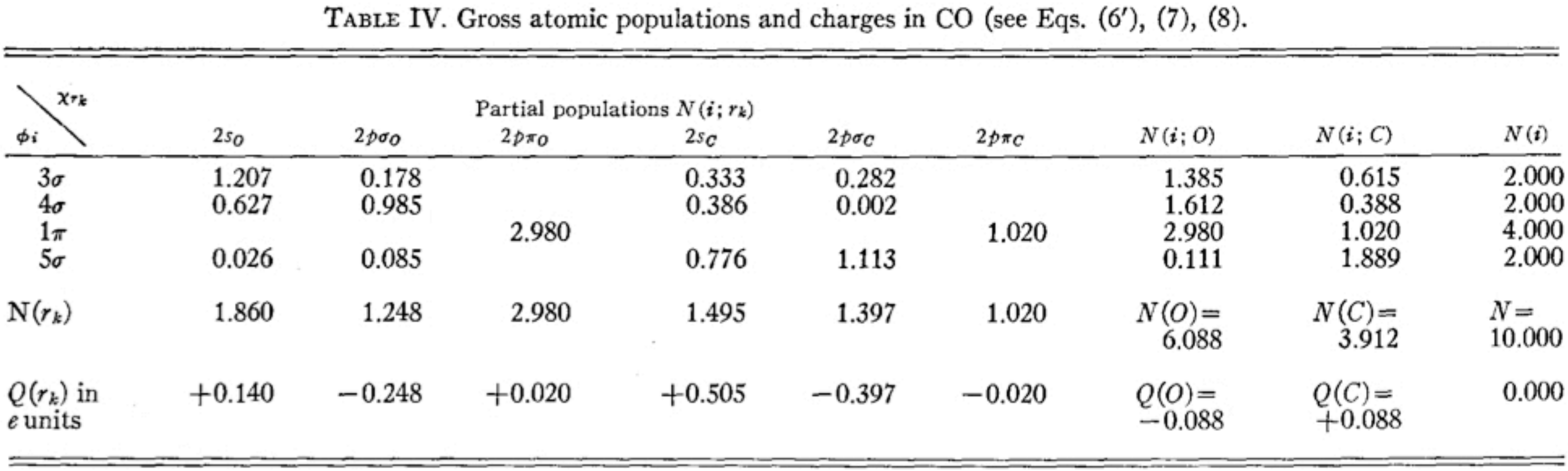


TABLE IV. Gross atomic populations and charges in CO (see Eqs. (6′), (7), (8).

ϕ_i \ χ_{r_k}	Partial populations $N(i; r_k)$								
	$2s_O$	$2p\sigma_O$	$2p\pi_O$	$2s_C$	$2p\sigma_C$	$2p\pi_C$	$N(i; O)$	$N(i; C)$	$N(i)$
3σ	1.207	0.178		0.333	0.282		1.385	0.615	2.000
4σ	0.627	0.985		0.386	0.002		1.612	0.388	2.000
1π			2.980			1.020	2.980	1.020	4.000
5σ	0.026	0.085		0.776	1.113		0.111	1.889	2.000
$N(r_k)$	1.860	1.248	2.980	1.495	1.397	1.020	$N(O)=6.088$	$N(C)=3.912$	$N=10.000$
$Q(r_k)$ in e units	+0.140	−0.248	+0.020	+0.505	−0.397	−0.020	$Q(O)=-0.088$	$Q(C)=+0.088$	0.000

Using the gross atomic populations, we find:	Gross Charge
On the Carbon(N_0 = 4): $N(C)$ = 3.912	-0.088e
On the Oxygen(N_0 = 6): $N(O)$ = 6.088	+0.088e

The CO molecule has a small dipole moment in the direction of Oxygen.

An example: CO

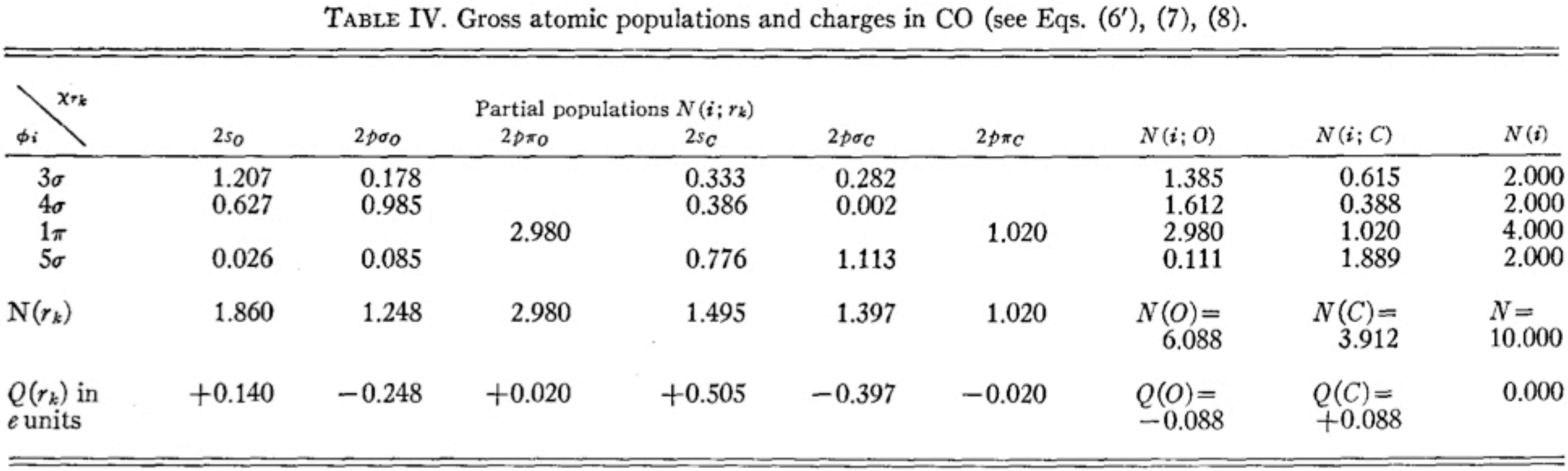


TABLE IV. Gross atomic populations and charges in CO (see Eqs. (6′), (7), (8).

ϕ_i \ χ_{r_k}	Partial populations $N(i; r_k)$								
	$2s_O$	$2p\sigma_O$	$2p\pi_O$	$2s_C$	$2p\sigma_C$	$2p\pi_C$	$N(i; O)$	$N(i; C)$	$N(i)$
3σ	1.207	0.178		0.333	0.282		1.385	0.615	2.000
4σ	0.627	0.985		0.386	0.002		1.612	0.388	2.000
1π			2.980			1.020	2.980	1.020	4.000
5σ	0.026	0.085		0.776	1.113		0.111	1.889	2.000
$N(r_k)$	1.860	1.248	2.980	1.495	1.397	1.020	$N(O) =$ 6.088	$N(C) =$ 3.912	$N =$ 10.000
$Q(r_k)$ in e units	+0.140	−0.248	+0.020	+0.505	−0.397	−0.020	$Q(O) =$ −0.088	$Q(C) =$ +0.088	0.000

Using the gross atomic populations, we find:

1π orbital: *N(C)* = 1.020; *N(O)* = 2.980

The pi orbital sits primarily on the Oxygen atom (C^+O^- polarization).

An example: CO

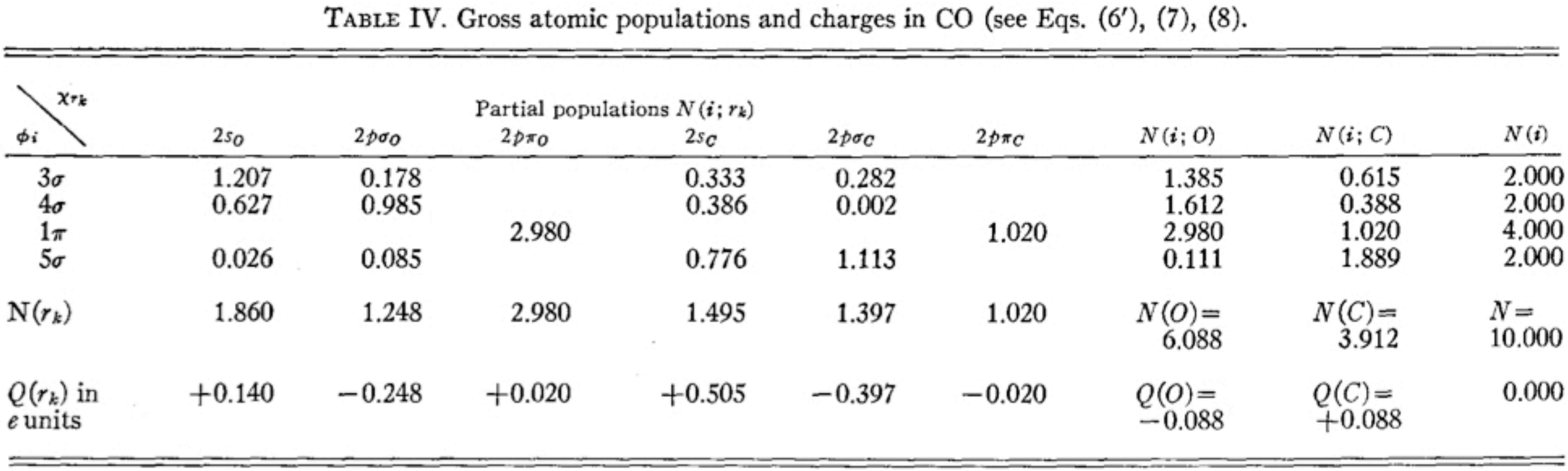


TABLE IV. Gross atomic populations and charges in CO (see Eqs. (6′), (7), (8).

ϕ_i \ χ_{r_k}	Partial populations $N(i;r_k)$								
	$2s_O$	$2p\sigma_O$	$2p\pi_O$	$2s_C$	$2p\sigma_C$	$2p\pi_C$	$N(i;O)$	$N(i;C)$	$N(i)$
3σ	1.207	0.178		0.333	0.282		1.385	0.615	2.000
4σ	0.627	0.985		0.386	0.002		1.612	0.388	2.000
1π			2.980			1.020	2.980	1.020	4.000
5σ	0.026	0.085		0.776	1.113		0.111	1.889	2.000
$N(r_k)$	1.860	1.248	2.980	1.495	1.397	1.020	$N(O)=$ 6.088	$N(C)=$ 3.912	$N=$ 10.000
$Q(r_k)$ in e units	+0.140	−0.248	+0.020	+0.505	−0.397	−0.020	$Q(O)=$ −0.088	$Q(C)=$ +0.088	0.000

Using the gross atomic populations, we find:

5σ orbital: $N(C) = 1.889$; $N(O) = 0.111$

The HOMO sits primarily on the Carbon atom (C^-O^+ polarization).

CO forms strong bonds in metal complexes such as $Fe(CO)_5$.
Bonding occurs through the Carbon atom end, but uses π^* orbitals.

An example: CO

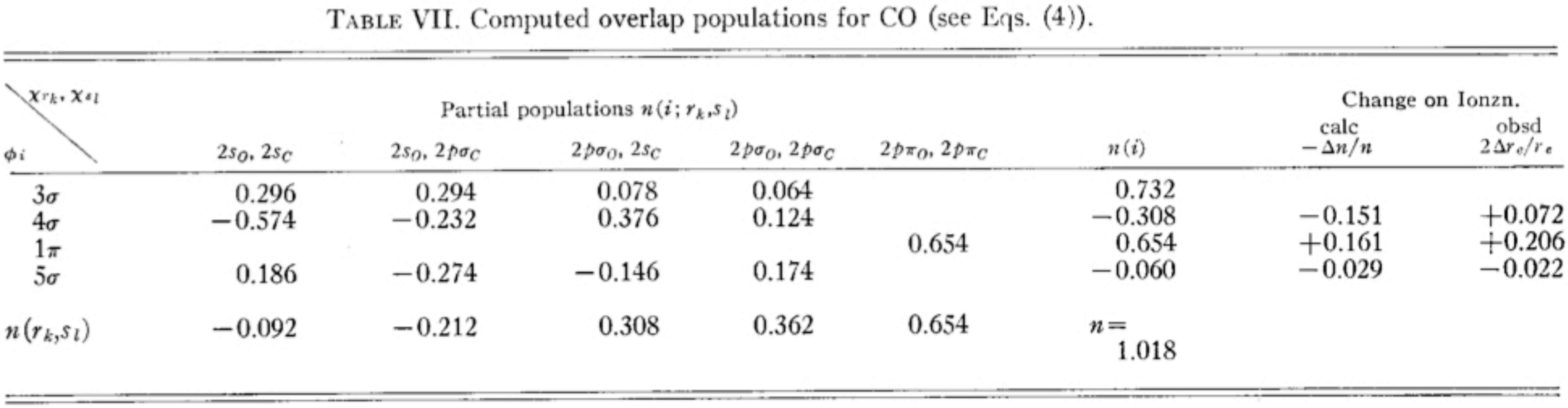


TABLE VII. Computed overlap populations for CO (see Eqs. (4)).

χ_{r_k}, χ_{s_l} / ϕ_i	Partial populations $n(i; r_k, s_l)$						Change on Ionzn.	
	$2s_O, 2s_C$	$2s_O, 2p\sigma_C$	$2p\sigma_O, 2s_C$	$2p\sigma_O, 2p\sigma_C$	$2p\pi_O, 2p\pi_C$	$n(i)$	calc $-\Delta n/n$	obsd $2\Delta r_e/r_e$
3σ	0.296	0.294	0.078	0.064		0.732		
4σ	−0.574	−0.232	0.376	0.124		−0.308	−0.151	+0.072
1π					0.654	0.654	+0.161	+0.206
5σ	0.186	−0.274	−0.146	0.174		−0.060	−0.029	−0.022
$n(r_k, s_l)$	−0.092	−0.212	0.308	0.362	0.654	$n=$ 1.018		

Using the overlap populations, we find:

3σ (σ_{2s}) overlap population = 0.732
4σ (σ^*_{2s}) overlap population = -0.308
1π (π_{2p}) overlap population = 0.654
5σ (σ_{2p}) overlap population = -0.060

3σ and 1π are bonding orbitals.

4σ and 5σ are nonbonding orbitals!

An example: CO

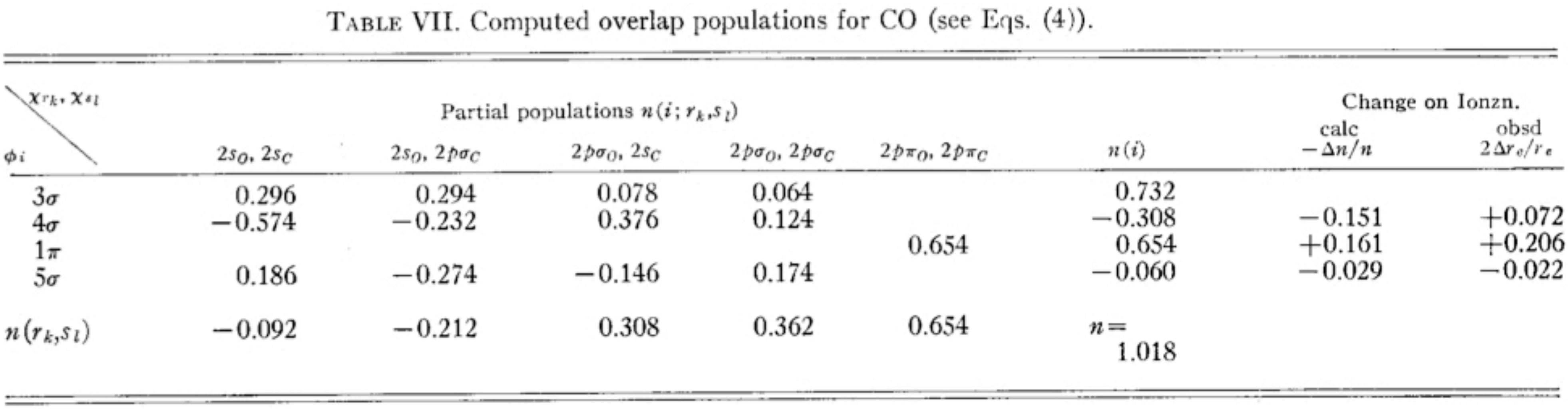


TABLE VII. Computed overlap populations for CO (see Eqs. (4)).

ϕ_i \ χ_{r_k}, χ_{s_l}	Partial populations $n(i; r_k, s_l)$						Change on Ionzn.	
	$2s_O, 2s_C$	$2s_O, 2p\sigma_C$	$2p\sigma_O, 2s_C$	$2p\sigma_O, 2p\sigma_C$	$2p\pi_O, 2p\pi_C$	$n(i)$	calc $-\Delta n/n$	obsd $2\Delta r_e/r_e$
3σ	0.296	0.294	0.078	0.064		0.732		
4σ	−0.574	−0.232	0.376	0.124		−0.308	−0.151	+0.072
1π					0.654	0.654	+0.161	+0.206
5σ	0.186	−0.274	−0.146	0.174		−0.060	−0.029	−0.022
$n(r_k, s_l)$	−0.092	−0.212	0.308	0.362	0.654	$n=$ 1.018		

Using the overlap populations, we find:

3σ (σ_{2s}) overlap population = 0.732
4σ (σ^*_{2s}) overlap population = -0.308
1π (π_{2p}) overlap population = 0.654
5σ (σ_{2p}) overlap population = -0.060

σ overlap: 0.364

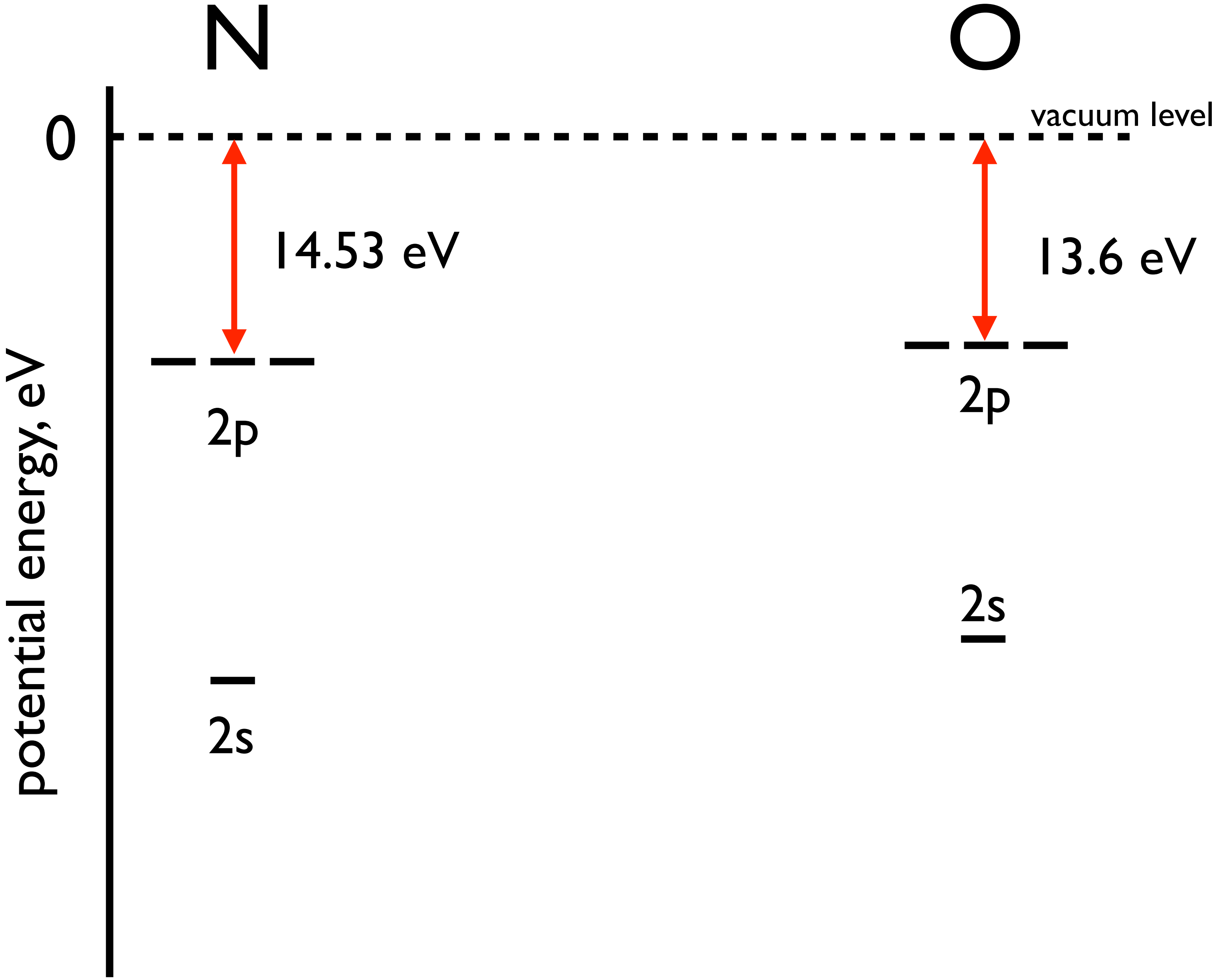
π overlap: 0.654

(1 σ and 2 π bonds)

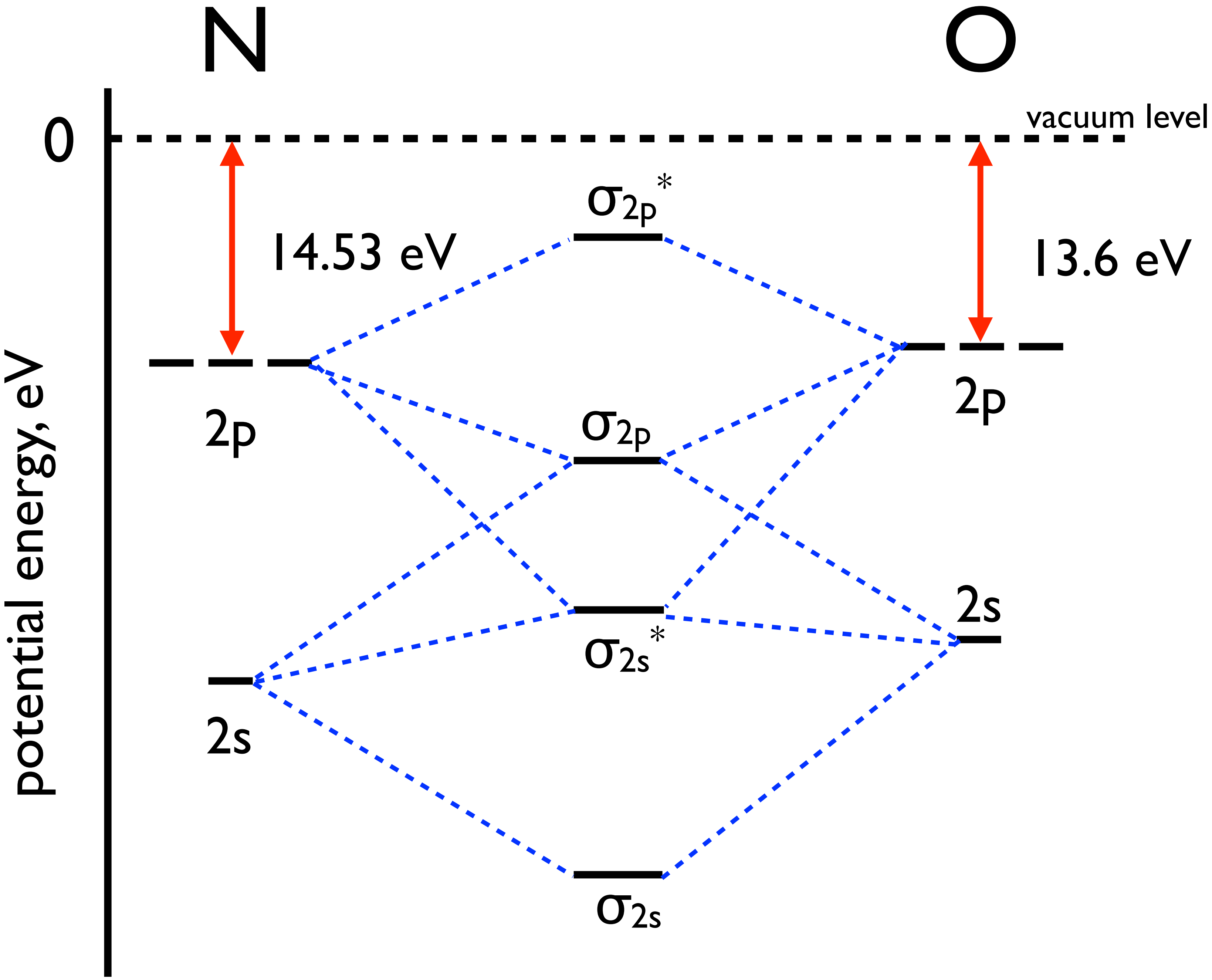
Total overlap: 1.018 (80% of N_2 =1.276)

a triple bond

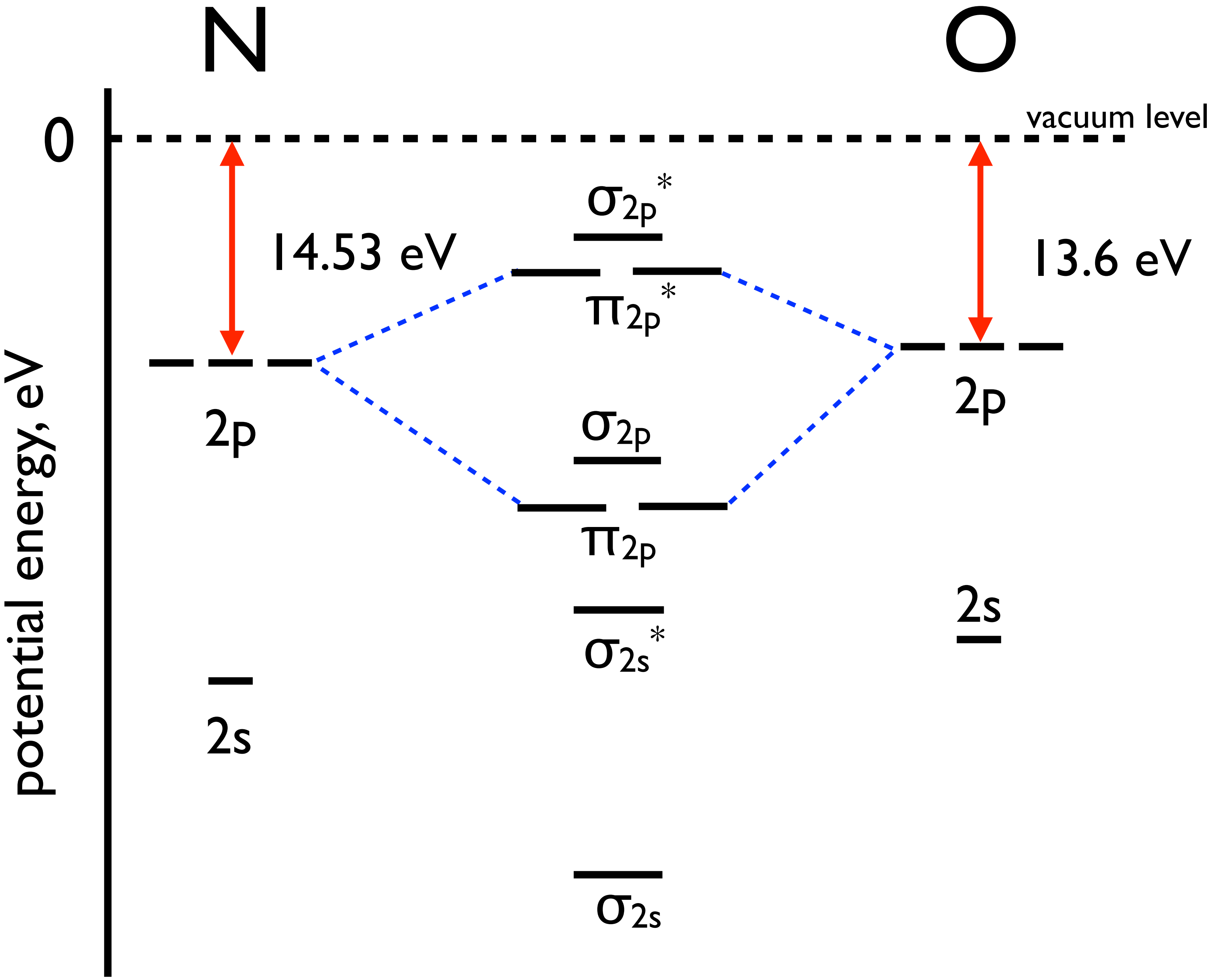
A final example: Nitric Monoxide (NO)



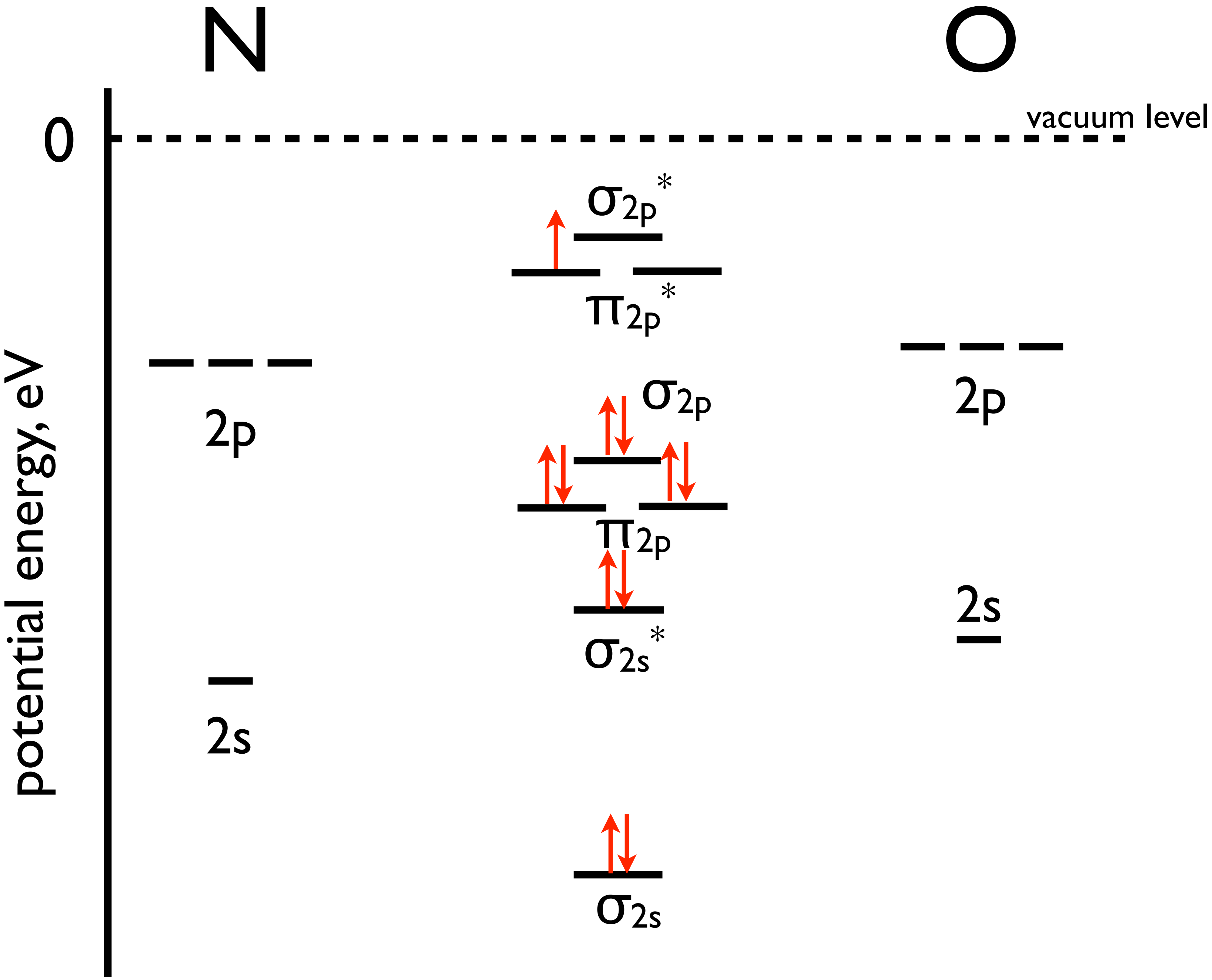
A final example: Nitric Monoxide (NO)



A final example: Nitric Monoxide (NO)



A final example: Nitric Monoxide (NO) - 11 electrons



A final example: Nitric Monoxide (NO) - 11 electrons

For NO:

bond order = **2.5**

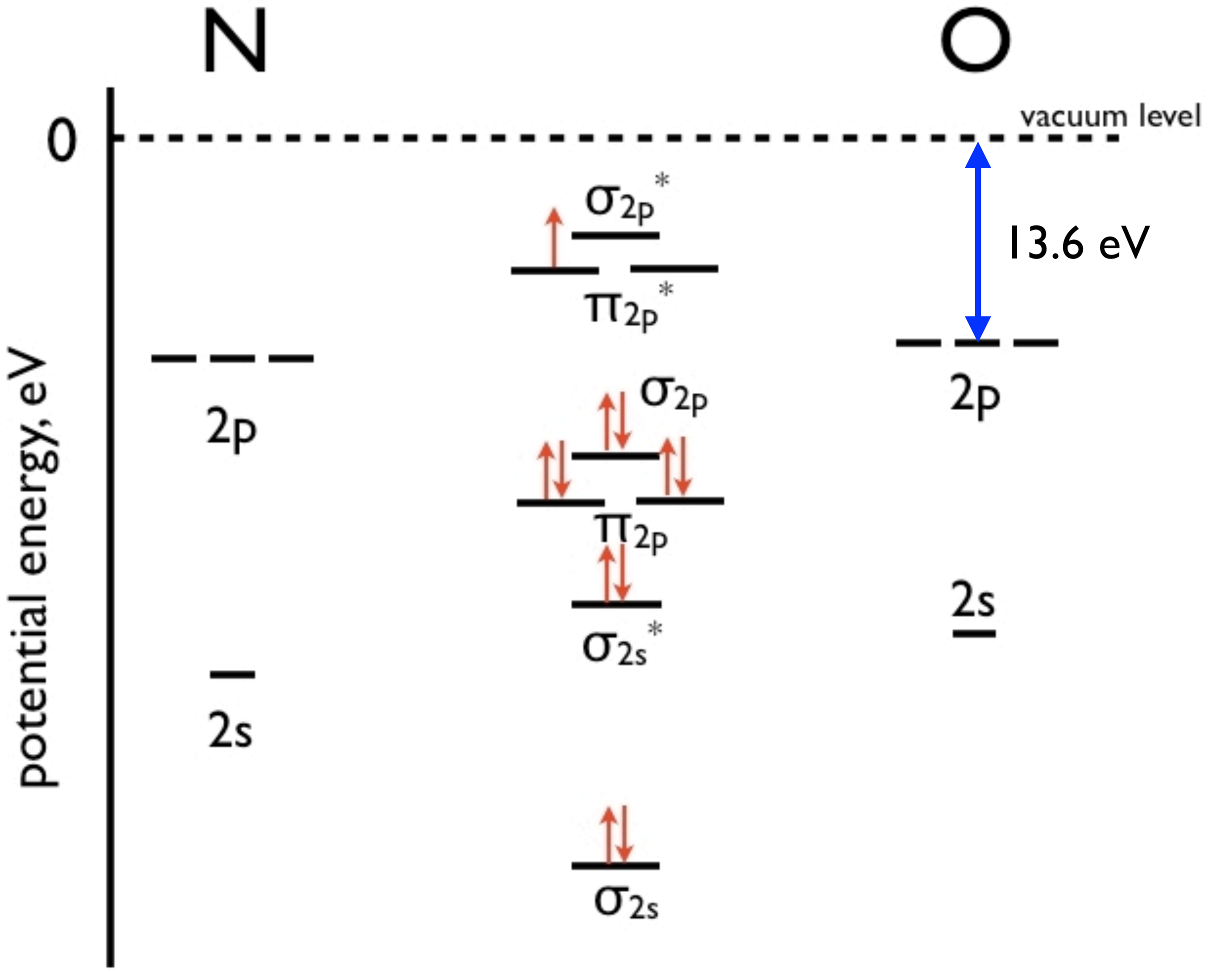
NO is **paramagnetic**

IP is less than 13.6 eV

Electron configuration is:

$\sigma_{2s}^2\,\sigma^*_{2s}{}^2\,\pi_{2p}{}^4\sigma_{2p}{}^2\pi^*_{2p}{}^1$

One electron in the HOMO



The fool-proof procedure for constructing energy correlation diagrams:

0. Draw the vacuum level.
1. Put the atomic orbitals for each bonding partner in your diagram. *Position the HOAO based upon the IP of the atom.*
2. Draw in the energy levels for your MOs. *You'll need one for each atomic state.*
3. Fill them with electrons. *Make sure to follow Aufbau and Hund's rules.*

Easy as Toast!

Another example: H_2O

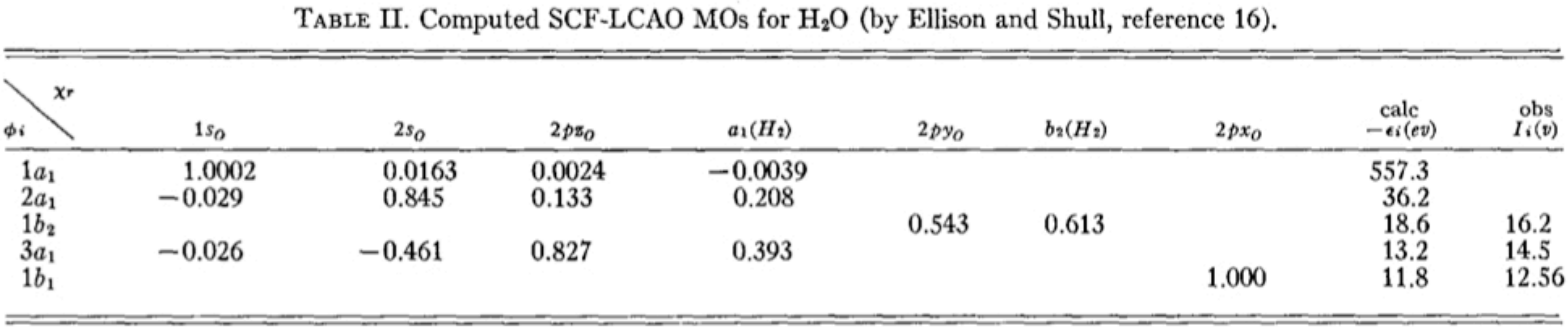


TABLE II. Computed SCF-LCAO MOs for H_2O (by Ellison and Shull, reference 16).

$\phi_i \backslash \chi_r$	$1s_O$	$2s_O$	$2pz_O$	$a_1(H_2)$	$2py_O$	$b_2(H_2)$	$2px_O$	calc $-\epsilon_i(ev)$	obs $I_i(v)$
$1a_1$	1.0002	0.0163	0.0024	−0.0039				557.3	
$2a_1$	−0.029	0.845	0.133	0.208				36.2	
$1b_2$					0.543	0.613		18.6	16.2
$3a_1$	−0.026	−0.461	0.827	0.393				13.2	14.5
$1b_1$							1.000	11.8	12.56

Nomenclature: Mulliken includes 1s MOs:

Ours (8 electrons): $1a_1^2\ 1b_2^2\ 2a_1^2\ 1b_1^2$

His (10 electrons): $1a_1^2\ 2a_1^2\ 1b_2^2\ 3a_1^2\ 1b_1^2$

Another example: H_2O

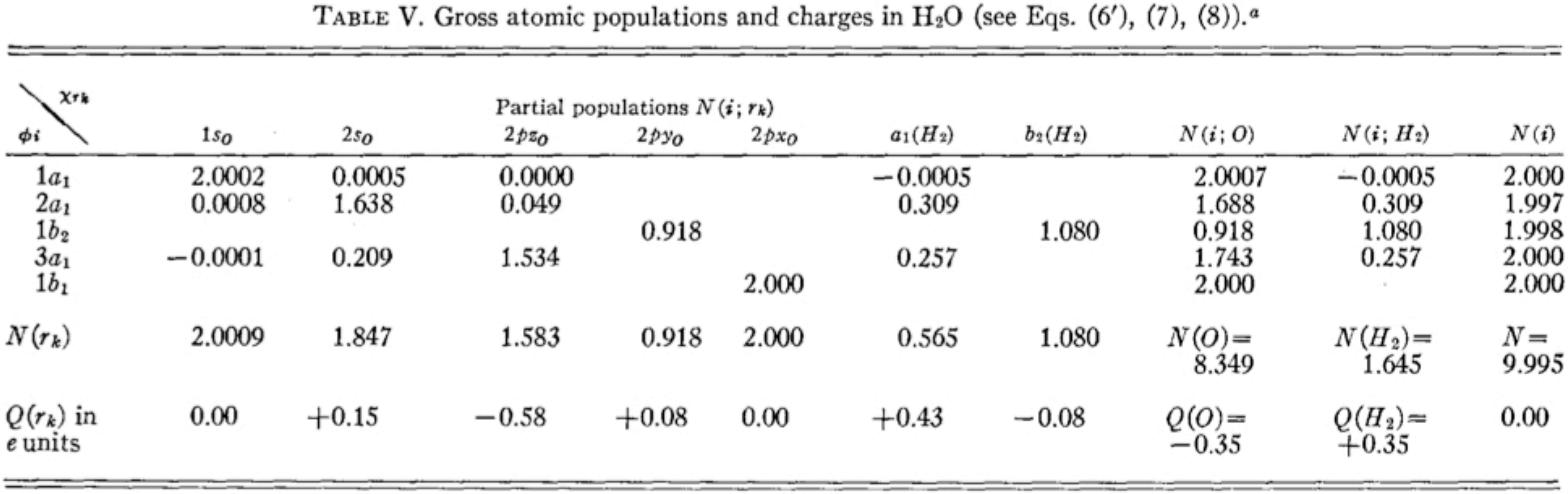


TABLE V. Gross atomic populations and charges in H_2O (see Eqs. (6′), (7), (8)).[a]

χ_{r_k} / ϕ_i	Partial populations $N(i; r_k)$									
	$1s_O$	$2s_O$	$2pz_O$	$2py_O$	$2px_O$	$a_1(H_2)$	$b_2(H_2)$	$N(i; O)$	$N(i; H_2)$	$N(i)$
$1a_1$	2.0002	0.0005	0.0000			−0.0005		2.0007	−0.0005	2.000
$2a_1$	0.0008	1.638	0.049			0.309		1.688	0.309	1.997
$1b_2$				0.918			1.080	0.918	1.080	1.998
$3a_1$	−0.0001	0.209	1.534			0.257		1.743	0.257	2.000
$1b_1$					2.000			2.000		2.000
$N(r_k)$	2.0009	1.847	1.583	0.918	2.000	0.565	1.080	$N(O)=$ 8.349	$N(H_2)=$ 1.645	$N=$ 9.995
$Q(r_k)$ in e units	0.00	+0.15	−0.58	+0.08	0.00	+0.43	−0.08	$Q(O)=$ −0.35	$Q(H_2)=$ +0.35	0.00

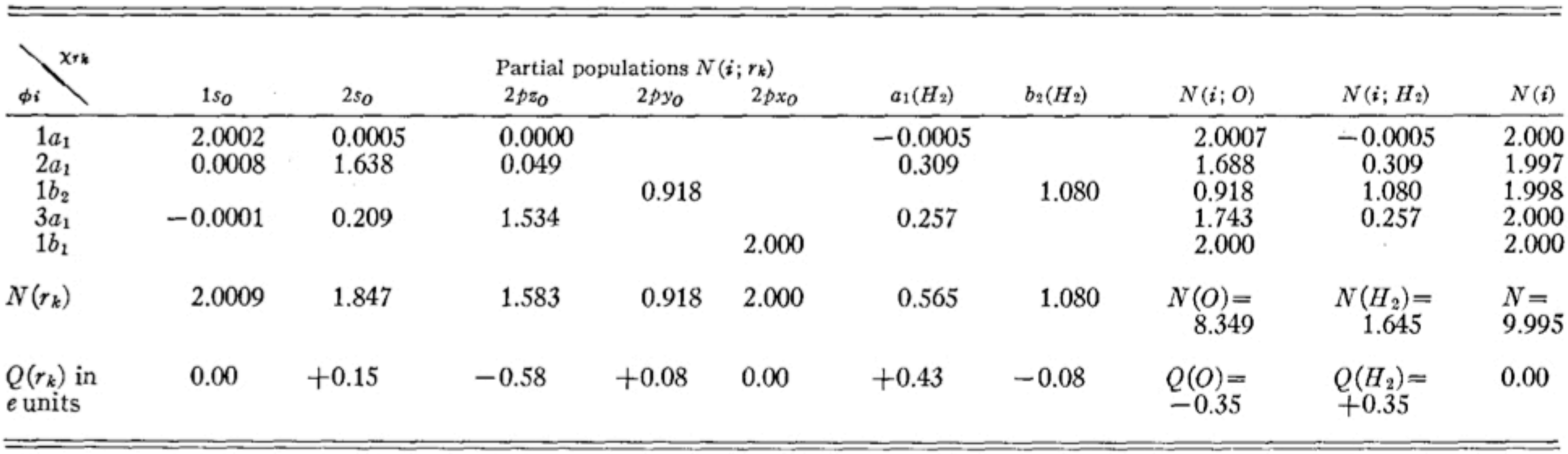
Using the gross atomic populations, we find:

atomic populations: Oxygen: $1s^{2.00}2s^{1.85}2p^{4.50}$

Hydrogens (each): $1s^{0.82}$

Another example: H_2O

TABLE V. Gross atomic populations and charges in H_2O (see Eqs. (6′), (7), (8)).[a]



ϕ_i \ χ_{r_k}	Partial populations $N(i; r_k)$									
	$1s_O$	$2s_O$	$2pz_O$	$2py_O$	$2px_O$	$a_1(H_2)$	$b_2(H_2)$	$N(i; O)$	$N(i; H_2)$	$N(i)$
$1a_1$	2.0002	0.0005	0.0000			−0.0005		2.0007	−0.0005	2.000
$2a_1$	0.0008	1.638	0.049			0.309		1.688	0.309	1.997
$1b_2$				0.918			1.080	0.918	1.080	1.998
$3a_1$	−0.0001	0.209	1.534			0.257		1.743	0.257	2.000
$1b_1$					2.000			2.000		2.000
$N(r_k)$	2.0009	1.847	1.583	0.918	2.000	0.565	1.080	$N(O)=$ 8.349	$N(H_2)=$ 1.645	$N=$ 9.995
$Q(r_k)$ in e units	0.00	+0.15	−0.58	+0.08	0.00	+0.43	−0.08	$Q(O)=$ −0.35	$Q(H_2)=$ +0.35	0.00

Using the gross atomic populations, we find:

		Gross Charge
On the Oxygen ($N_0 = 8$):	$N(O) = 8.349$	-0.35e
On the Hydrogens ($N_0 = 2$):	$N(H_2) = 1.645$	+0.35e

Another example: H_2O

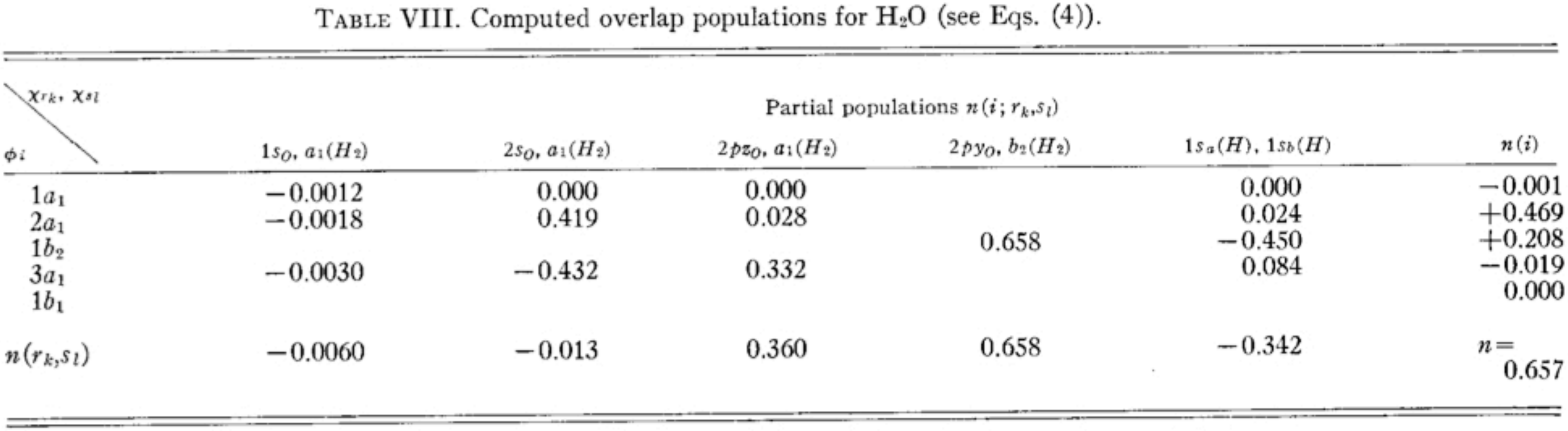


TABLE VIII. Computed overlap populations for H_2O (see Eqs. (4)).

χ_{r_k}, χ_{s_l} / ϕ_i	Partial populations $n(i; r_k, s_l)$					
	$1s_O, a_1(H_2)$	$2s_O, a_1(H_2)$	$2pz_O, a_1(H_2)$	$2py_O, b_2(H_2)$	$1s_a(H), 1s_b(H)$	$n(i)$
$1a_1$	−0.0012	0.000	0.000		0.000	−0.001
$2a_1$	−0.0018	0.419	0.028		0.024	+0.469
$1b_2$				0.658	−0.450	+0.208
$3a_1$	−0.0030	−0.432	0.332		0.084	−0.019
$1b_1$						0.000
$n(r_k, s_l)$	−0.0060	−0.013	0.360	0.658	−0.342	$n =$ 0.657

Bonding occurs through the $2a_1$ and $1b_2$ orbitals. The higher energy $3a_1$ and $1b_1$ do not contribute to the bonding.