Hartree-Fock equations

Note Title 4/1/2015

Aim

- derive the necessary equations for obtaining E_e (and E_{tot}) as well as χ_i s. (MOs)

How?

→ find the orthonormal MOs which deliver the minimum E_e

→ **constrained optimization**

→ method of Lagrange undetermined multipliers (MLUM)

MLUM

- construct the function to be optimized:

$$f(x_1, x_2, \dots, x_N)$$

- define the constraint condition

$$g(x_1, x_2, \dots, x_N)$$

- construct the Lagrange function

$$L(x_1, x_2, \dots, x_N) = f(x_1, x_2, \dots, x_N) - \lambda \cdot g(x_1, x_2, \dots, x_N)$$

where:

λ = constant (Lagrange multiplier)

- can be given a physical interpretation
- one multiplier is added for each constraint

- impose:

$$\delta L = 0 \qquad \left(\text{optimize } L \text{ such that } \frac{\partial L}{\partial x_i} = 0 \text{ and } \frac{\partial L}{\partial \lambda} = 0\right)$$

L function is optimized by requiring that the gradient with respect to x and λ is zero

Example (see Leach, 1.10.5, pg. 18)

$f(x,y) = 4x^2 + 3x + 2y^2 + 6y$ – function

$y = 4x + 2$ – constraint

Constraint must be written:

$$g(x,y) = 0 \quad \Rightarrow \quad g(x,y) = y - 4x - 2$$

$$L = f - \lambda g$$

$$dL = df - \lambda dg = 0$$

But:

$$df = \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy$$

$$dg = \frac{\partial g}{\partial x} dx + \frac{\partial g}{\partial y} dy$$

$$\Rightarrow \left[\frac{\partial f}{\partial x} - \lambda \frac{\partial g}{\partial x}\right] dx + \left[\frac{\partial f}{\partial y} - \lambda \frac{\partial g}{\partial y}\right] dy = 0$$

But:

$$\frac{\partial f}{\partial x} = (8x+3) \qquad \frac{\partial f}{\partial y} = 4y+6$$

$$\frac{\partial g}{\partial x} = -4 \qquad \frac{\partial g}{\partial y} = 1$$

$$\Rightarrow \begin{cases} 8x+3+4\lambda = 0 & (*) \\ 4y+6-\lambda = 0 & (**) \end{cases}$$

$(**) \times 4 + (*) \Rightarrow$

$$8x+3+16y+24 = 0 \quad \Rightarrow \quad x = -2y - \frac{27}{8} \quad (***)$$

Based on the constraint condition:

$$y = 4x+2 \xRightarrow{(***)} y = -8y - \frac{27}{2} + 2$$

$$\Rightarrow \boxed{y = -\frac{23}{18}} \xRightarrow{(***)} \boxed{x = -\frac{59}{72}} \text{ and } \xRightarrow{(**)} \boxed{\lambda = \frac{8}{9}}$$

In our case:

$$f = E_e(\chi_i) = E_e[\chi_i]$$

$$g = ?$$

$$\langle \chi_i | \chi_j \rangle = \delta_{ij} \Rightarrow g \rightarrow g_{ij} = \langle \chi_i | \chi_j \rangle - \delta_{ij}$$

$\downarrow$

ε_{ij} – matrix of constants (symmetric)

– Lagrange multipliers

$$\Rightarrow \mathcal{L} = E_e - \sum_{ij} \varepsilon_{ij} [\langle \chi_i | \chi_j \rangle - \delta_{ij}]$$

double sum because all the χ_i, χ_j pairs must satisfy the $\langle \chi_i | \chi_j \rangle = \delta_{ij}$ condition

Now we impose the condition

$\delta \mathcal{L} = 0$ $\quad$ $\mathcal{L}$ – varied by varying the χ_i functions

$$\delta \mathcal{L} = \delta E_e - \sum_i \sum_j [\varepsilon_{ij} \delta (\langle \chi_i | \chi_j \rangle - \delta_{ij})]$$

But:

$\delta_{ij} = ct$ (0 or 1) $\Rightarrow \delta(\delta_{ij}) = 0$

$$\delta(\langle \chi_i | \chi_j \rangle) = \int [\delta \chi_i^*(1) \chi_j(1) + \underbrace{\chi_i^*(1) \delta \chi_j(1)}_{\text{complex conjugate of}}] d\tau_1$$

$$E_e = \sum_i \langle \chi_i | \hat{h}_i | \chi_i \rangle + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} [\langle \chi_i | \hat{J}_j | \chi_i \rangle - \langle \chi_i | \hat{K}_j | \chi_i \rangle]$$

with:

$$\hat{J}_j(1) | \chi_i(2) \rangle = \langle \chi_j(1) | \frac{1}{r_{12}} | \chi_j(1) \rangle | \chi_i(2) \rangle$$

$$K_j(1) | \chi_i(2) \rangle = \langle \chi_j(1) | \frac{1}{r_{12}} | \chi_i(1) \rangle | \chi_j(2) \rangle$$

$$\langle \chi_i(2) | J_j(1) | \chi_i(2) \rangle = \iint \chi_i^*(2) \chi_j^*(1) \frac{1}{r_{12}} \chi_j(1) \chi_i(2) d\tau_1 d\tau_2$$

$$\langle \chi_i(2) | J_j(1) | \chi_i(2) \rangle = \iint \chi_i^*(2) \chi_j^*(1) | \frac{1}{r_{12}} | \chi_i(1) \chi_j(2) d\tau_1 d\tau_2$$

Thus,

$$E_e = \sum_i \Big[\int \chi_i^*(1) \, | h(1) | \, \chi_i(1) \, d\tau_1 \; +$$

$$+ \frac{1}{2} \sum_i \sum_j \Big[\iint \chi_i^*(2) \chi_j^*(1) \frac{1}{r_{12}} \chi_j(1) \chi_i(2) \, d\tau_1 \, d\tau_2$$

$$- \frac{1}{2} \sum_i \sum_j \Big[\iint \chi_i^*(2) \chi_j^*(1) \, \Big| \frac{1}{r_{12}} \Big| \, \chi_i(1) \chi_j(2) \, d\tau_1 \, d\tau_2$$

Then:

$$\delta E_e =$$

$$= \sum_i \int \Big[\delta \chi_i^*(1) \, h(1) \chi_i(1) + \chi_i^*(1) \, h(1) \, \delta \chi_i(1) \Big] d\tau_1 \qquad t_0 + t_0^*$$

$$+ \frac{1}{2} \sum_{ij} \iint \delta \chi_i^*(2) \chi_j^*(1) \frac{1}{r_{12}} \chi_j(1) \chi_i(2) \, d\tau_1 \, d\tau_2 \qquad t_1$$

$$+ \frac{1}{2} \sum_{ij} \iint \chi_i^*(2) \chi_j^*(1) \frac{1}{r_{12}} \delta \chi_i^*(2) \, \chi_j(1) \, d\tau_1 \, d\tau_2 \qquad t_2 = t_1^*$$

$$+ \frac{1}{2} \sum_{ij} \iint \chi_i^*(2) \, \delta \chi_j^*(1) \frac{1}{r_{12}} \chi_j(1) \chi_i(2) \, d\tau_1 \, d\tau_2 \qquad t_3$$

$$+ \frac{1}{2} \sum_{ij} \iint \chi_i^*(2) \chi_j^*(1) \frac{1}{r_{12}} \chi_j(1) \, \delta \chi_i(2) \, d\tau_1 \, d\tau_2 \qquad t_4 = t_3^*$$

$$- \frac{1}{2} \sum_{ij} \iint \delta \chi_i^*(2) \chi_j^*(1) \frac{1}{r_{12}} \chi_i(1) \chi_j(2) \, d\tau_1 \, d\tau_2 \qquad t_5$$

$$- \frac{1}{2} \sum_{ij} \iint \chi_i^*(2) \chi_j^*(1) \frac{1}{r_{12}} \delta \chi_i(1) \chi_j(2) \, d\tau_1 \, d\tau_2 \qquad t_6 = t_5^*$$

$$- \frac{1}{2} \sum_{ij} \iint \chi_i^*(2) \, \delta \chi_j^*(1) \frac{1}{r_{12}} \chi_i(1) \chi_j(2) \, d\tau_1 \, d\tau_2 \qquad t_7$$

$$- \frac{1}{2} \sum_{ij} \iint \chi_i^*(2) \chi_j^*(1) \frac{1}{r_{12}} \chi_i(1) \, \delta \chi_j(2) \, d\tau_1 \, d\tau_2 \qquad t_8 = t_7^*$$

But: $t_3 = t_1 \quad t_4 = t_2 \quad t_7 = t_5 \quad t_8 = t_6$

(see this by changing $1 \leftrightarrow 2$ & $i \leftrightarrow j$)

$$\Rightarrow \quad \delta E_e = \sum_i \left[t_0 + t_0^* \right] + \frac{1}{2} \sum_{ij} \left[2t_1 + 2t_1^* - 2t_5 - 2t_5^* \right]$$

$$= \sum_i t_0 + \sum_{ij} t_1 - \sum_{ij} t_5 +$$

$$+ \sum_i t_0^* + \sum_{ij} t_1^* - \sum_{ij} t_5^*$$

That is:

$$\delta E_e = \sum_i \int \delta \chi_i^*(1)\, h(1)\, \chi_i(1)\, d\tau_1$$

$$+ \sum_{ij} \iint \delta \chi_i^*(\underset{1}{2})\, \chi_j^*(\underset{2}{1})\, \frac{1}{r_{12}}\, \chi_j(\underset{2}{1})\, \chi_i(\underset{1}{2})\, d\tau_1\, d\tau_2$$

$$- \sum_{ij} \iint \delta \chi_i^*(\underset{1}{2})\, \chi_j^*(\underset{2}{1})\, \frac{1}{r_{12}}\, \chi_i(\underset{2}{1})\, \chi_j(\underset{1}{2})\, d\tau_1\, d\tau_2$$

+ the complex conjugate

Now,

$$\sum_{ij} \varepsilon_{ij}\, \delta(\langle \chi_i | \chi_j \rangle) = \sum_{ij} \varepsilon_{ij} \int \delta \chi_i^*(1)\, \chi_j(1)\, d\tau_1 + \text{complex conjugate}$$

$$\Rightarrow \delta \mathcal{L} = \sum_i \int \delta \chi_i^*(1) \Big[h(1)\, \chi_i(1) + \sum_j \int \chi_j^*(2)\, \frac{1}{r_{12}}\, \chi_j(2)\, \chi_i(1)\, d\tau_2$$

$$- \sum_j \int \chi_j^*(2)\, \frac{1}{r_{12}}\, \chi_i(2)\, \chi_j(1)\, d\tau_2$$

$$- \sum_j \varepsilon_{ij}\, \chi_j(1) \Big]\, d\tau_1$$

+ complex conjugate

$$\Rightarrow \delta \mathcal{L} = \sum_i \int \delta \chi_i^*(1) \left\{ h(1)\, \chi_i(1) + \sum_j \left[J_j(2) - K_j(2) \right] \chi_i(1) - \sum_j \varepsilon_{ij}\, \chi_j(1) \right\} d\tau_1$$

+ complex conjugate

Imposing: $\delta \mathcal{L} = 0 \Rightarrow \{ \dots \} = 0$ (because $\delta \chi_i^*(1)$ - arbitrary)

$\rightarrow$ analogous for the c.c. term

Finally:

$$\underbrace{\left\{ h(1) + \sum_j \left[J_j(1) - K_j(1) \right] \right\}}_{\text{Fock operator } F(1)} \chi_i(1) = \sum_j \varepsilon_{ij} \chi_j(1)$$

$$\hat{F}(i) = h(i) + \sum_j \left[\hat{J}_j(i) - \hat{K}_j(i) \right]$$

- monoelectronic operator
- describes the kinetic energy of an e^- and its attraction by the nuclei (through $\hat{h}_i$) and the electrostatic repulsion due to all the other electrons (through $\hat{J}_j$ and $\hat{K}_j$)

Define:

$$\hat{V}_{HF}(i) = \sum_j \left[\hat{J}_j - \hat{K}_j \right]$$ – Hartree-Fock operator

- average repulsive potential felt by the electron "i", due to all the other N-1 e^-s.
- replaces the exact bielectronic operator $1/r_{12}$ through an averaged monoelectronic operator

$$\hat{V}_{HF}(i) | \chi_i \rangle = \sum_j \left[\hat{J}_j - \hat{K}_j \right] | \chi_i \rangle$$

Summing up:

$$\boxed{\hat{F}_i \chi_i = \sum_j \varepsilon_{ij} \chi_i \qquad i = \overline{1,N}}$$

- first version of the HF equations
- not a standard eigenvalue problem (because of ε_{ij} terms)

ε_{ij} can be diagonalized through a unitary transformation

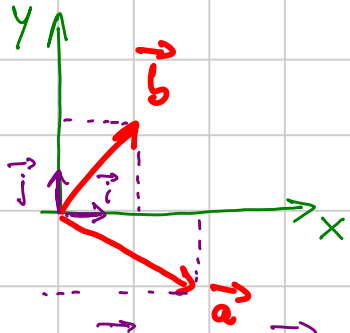
Find a matrix U, so that:

$$U^+ \varepsilon U = \varepsilon'$$

$\hookrightarrow$ diagonal matrix

χ_i functions transform as:

$$\chi_i' = \sum_j \chi_j U_{ij}$$



$\vec{a} = a_x \cdot \vec{i} + a_y \cdot \vec{j}$

$\vec{b} = b_x \vec{i} + b_y \cdot \vec{j}$

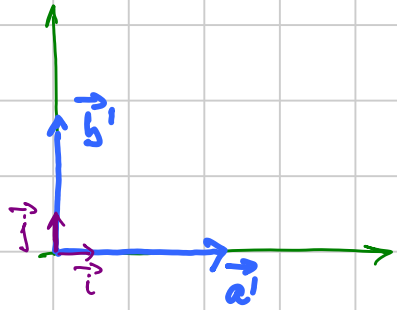
$\hat{F}$ – invariant to a unitary transform

χ' – diagonalize the ε_{ij} matrix

– **canonical orbitals**

– standards typical

$$\boxed{F_i \chi_i = \varepsilon_i \chi_i}$$



$a' = a_x \cdot \vec{i} + 0$

$b' = 0 + b_y \cdot \vec{j}$

– HF equations

– a set of N non linear eqs

– an alternative to the Schrödinger eq.

(the exact $\hat{H}$ is replaced by an approximative Fock operator)

Obs:

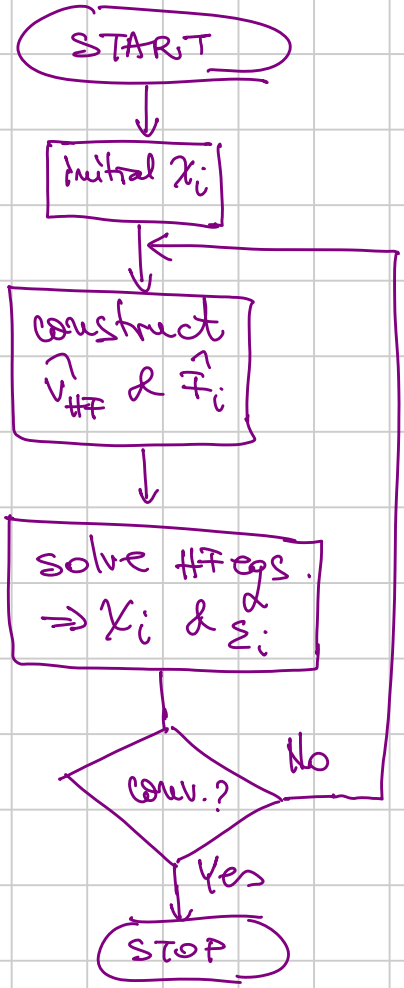
$\hat{F}$ depends on χ_i (through $\hat{J}$ & $\hat{K}$)

solution: SCF iterations with guessed χ_is

χ_i - SCF orbitals

ε_i - eigenvalues of HF eqs.

- MO energies



Meaning of ε_i

Express E_e in terms of ε_i:

Start with HF eqs.:

$$\hat{F}_i \chi_i = \varepsilon_i |\chi_i\rangle \qquad \Big| \cdot \chi_i \text{ \& integrate}$$

$$\Rightarrow \langle \chi_i | \varepsilon_i | \chi_i \rangle = \langle \chi_i | \hat{F}_i | \chi_i \rangle$$

$$\varepsilon_i \langle \chi_i | \chi_i \rangle = \varepsilon_i = \langle \chi_i | h_i + \sum_j [J_j - K_j] | \chi_i \rangle$$

$$= \langle \chi_i | h_i | \chi_i \rangle + \sum_j \langle \chi_i | J_j - K_j | \chi_i \rangle$$

$$\Rightarrow \varepsilon_i = H_i + \sum_j (J_{ij} - K_{ij})$$

$$\Rightarrow H_i = \varepsilon_i - \sum_j (J_{ij} - K_{ij}) \text{ and } \sum_i H_i = \sum \varepsilon_i - \sum_i \sum_j (J_{ij} - K_{ij}) \quad (*)$$

E_e was:

$$E_e = \sum_i H_i + \frac{1}{2} \sum_i \sum_j (J_{ij} - K_{ij})$$

Replacing $\sum_i H_i$ by $(*)$ $\Rightarrow$

$$E_e = \sum \varepsilon_i - \frac{1}{2} \sum_i \sum_j (J_{ij} - K_{ij})$$

that is,

$$E_e \neq \sum \varepsilon_i$$

Why?

- ε_i – contains the interaction of e^- "i" with all the others
- ε_j — " — — " — "j" — " —

$\Rightarrow$ $i \leftrightarrow j$ interaction is considered twice in $\sum_i \varepsilon_i$

So, what is ε_i ?

(1) Consider the ionization of the molecule:

$$|^N\Psi\rangle \longrightarrow |^{N-1}\Psi_k\rangle = |\chi_1, \dots, \chi_{k-1}, \chi_k, \dots \chi_N\rangle$$

- ionization from MO k
- "frozen approximation" χ_i – does not change

$$E^k_{N-1} = \sum_{\substack{i=1\\ i\neq k}}^{N} h_i + \frac{1}{2}\sum_{\substack{i=1\\ i\neq k}}^{N}\sum_{\substack{j=1\\ j\neq k}}^{N}(J_{ij} - K_{ij})$$

Define:

$$IP^k = E^k_{N-1} - E_N$$

– ionization potential from MO k.

– ability to release an e^-

$$IP^k = E^k_{N-1} - E_N =$$

$$= \sum_{i\neq k} h_i + \frac{1}{2}\sum_{i\neq k}\sum_{j\neq k}(J_{ij} - K_{ij})$$

$$- \sum_i h_i - \frac{1}{2}\sum_i\sum_j (J_{ij} - K_{ij})$$

$$= -h_k - \underbrace{\sum_{l=1}^{N}(J_{kl} - K_{kl})}_{\text{interaction of } e^- \ k \text{ with all the others}}$$

(Missing terms in E^k_{N-1}:

$J_{1k} - K_{1k}, \dots, J_{k-1;k} - K_{k-1;k}, J_{k+1;k} - K_{k+1;k}, \dots J_{Nk} - K_{Nk},$

$J_{k1} - K_{k1}, \dots, J_{kk-1} - K_{kk-1}, J_{kk+1} - K_{kk+1}, \dots, J_{kN} - K_{kN}$

The terms $J_{kk} - K_{kk}$ do not appear but can be introduced since $J_{kk} - K_{kk} = 0$

Considering that $J_{kl} = J_{lk}$, $K_{kl} = K_{lk} \Rightarrow$ the factor $1/2$ in front of Σ disappear.)

On the other hand:

$$\varepsilon_k = +h_k + \sum_{j=1}^{N} (J_{kj} - K_{kj})$$

$$\Rightarrow \quad IP_v^k = -\varepsilon_k$$ – Koopmans' theorem

– can be measured by XPS, UPS
calculated as $-\varepsilon_k$

v – vertical (ionization potential)
– no change in the χ_i's
geometry of the molecule

$$IP_{ad} = E_{neutral} - E_{cation}$$

↳ adiabatic ionization potential
– involves the optimization of both, neutral molecule & cation

Electronic affinity

– the ability to receive an electron

Add an electron to one of the virtual spin-orbitals (let it be "r")

$$\Rightarrow |\Psi^N\rangle \longrightarrow |\Psi_r^{N+1}\rangle = |\chi_1 \chi_2 \dots \chi_N \chi_r\rangle$$

$$E_A = E^N - E_r^{N+1}$$

$$E^N = \sum_i^N h_i + \frac{1}{2} \sum_i^N \sum_j^N (J_{ij} - K_{ij})$$

$$E_r^{N+1} = \sum_i^{N+1} h_i + \frac{1}{2} \sum_i^{N+1} \sum_j^{N+1} (J_{ij} - K_{ij})$$

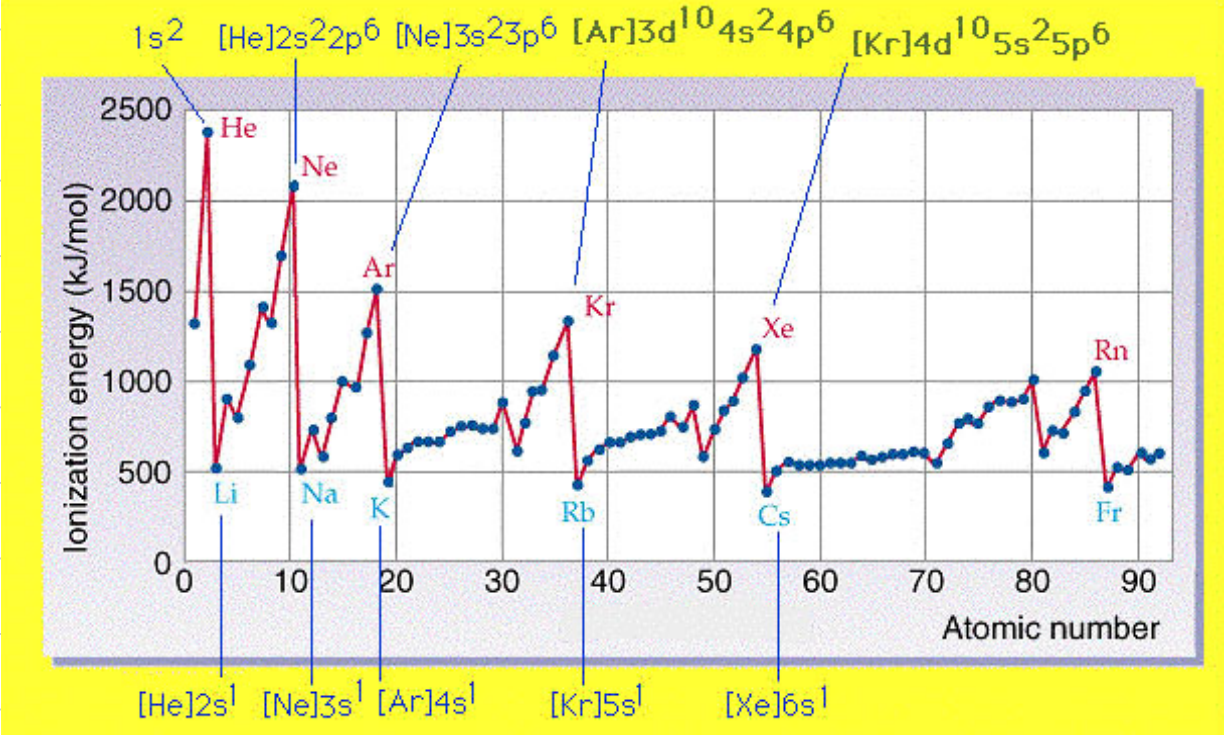
$$E_A = \underbrace{-H_r - \sum_{l=1}^{N+1} (J_{rl} - K_{rl})}_{= -\varepsilon_r}$$

$$\Rightarrow \quad EA = -\varepsilon_r$$

The energy ε_r of a virtual spin orbital is the module of the electron affinity for that orbital

<u>Frozen orbital approximation</u>

- MOs for $|\Psi^{N-1}\rangle$ and $|\Psi^{N+1}\rangle$ states are identical to those of the neutral state
- produces
  - too large IPs
  - too small EAs



http://www.iun.edu/~cpanhd/C101webnotes/modern-atomic-theory/ionization-energy.html

NIST: Atomic Spectra ×

physics.nist.gov/PhysRefData/ASD/ionEnergy.html

NIST Atomic Spectra Database Ionization Energies Form

Best viewed with the latest versions of Web browse

This form provides access to NIST critically evaluated data on ground states and ionization energies of atoms and atomic ions.

Spectra: O

e.g., Fe I *or* Na *or* H-Ds I *or* Mg+ *or* Al3+ *or* mg iv,vi-VIII; S V-xii *or* Fe ne-like-S-like *or* Ne-Fe I-III *or* Ni-like *or* H-like-Ne-like

Default Values | Retrieve Data

Units: eV

Format output: HTML (formatted)

Ordered by Z

Ordered by sequence

Output Data:

- [x] Atomic number
- [x] Spectrum name
- [x] Ion charge
- [x] Element name
- [x] Isoelectronic sequence
- [x] Ground-state electronic shells
- [ ] Ground-state configuration
- [x] Ground-state level
- [x] Ionized configuration

- (•) Ionization energy
- ( ) Total binding energy
- [x] Uncertainty

Bibliographic references: [x]

Default Values | Retrieve Data

Table 1 Electron affinity and ionization energy for molecules used in this study.

Molecule	Electron affinity (eV)	Ionization energy (eV)
Tetrakis(dimethylamino)ethylene (TDAE)		5.36
Tetramethyl-tetraselenafulvalene (TMTSF)		6.27
Tetrathiafulvalene (TTF)		6.40
Pentacene	1.392	6.58
Anthracene	0.56	7.36
3,5-Dinitrobenzonitrile	2.16	
C_{60}	2.65	
Tetracyano-*p*-quinodimethane (TCNQ)	2.80	9.50
Tetrafluorotetracyano-*p*-quinodimethane (F_4TCNQ)	3.38	