Electronic Separability Theory: Embedding, thermodynamics and electron density topology

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Conceptual map of the talk

**AIM**
- Quantum Theory of Atoms in Molecules
  - RWF. Bader

**Embedding**
- Cluster-in-the-lattice
  - (Evolution of Crystal Field Theory)

**Theory of Electronic Separability**
- **TES**
  - R. McWeeny
  - S. Huzinaga

**Crystal properties**
- (Equation of state, elastic properties, phase transitions ...)

**Topological partitioning of the energy**
I. The Theory of Electronic Separability

We assume that the system can be described as a set of weakly correlated electronic groups, \( \{A, B, C, \ldots\} \), each group being represented by an antisymmetric group function, \( \{\Phi_A(1..N_A), \Phi_B(1..N_B), \ldots\} \). The electronic wavefunction for the whole system is given by

\[
\Psi(1, \ldots N) = M \sum_p \hat{P}_p \Phi_A(1, \ldots N_A) \Phi_B(N_A+1, \ldots N_A+N_B) \ldots
\]  

where \( M \) is a normalization constant, \( \hat{P}_p \) is a permutation operator that changes the order of electrons, and \( \sum_p \) runs over all electron permutations that exchange electrons among groups. In other words, \( \sum_p \hat{P}_p \) enforces the antisymmetry of \( \Psi(1, \ldots N) \).

Examples of weakly correlated groups:

- core versus valence electrons in atoms and molecules,
- core vs. extended sea of electrons in alkaline metals,
- \( \sigma \) vs \( \pi \) electrons in conjugate polyenes,
- each ion can be regarded as a group for very ionic crystals.

It must be stressed that weak correlation does no imply a small interaction energy between groups.
Work with the group functions is much simplified by enforcing strong-orthogonality conditions:

\[
\int \Phi^*_R(x_1, x_2, x_3, \ldots) \Phi_S(x_1', x_2', x_3', \ldots) dx_1 = \delta_{RS},
\]  

(2)

\(x_i\) being the spatial and spin coordinates of electron \(i\). The total energy of the system is then

\[E = \sum_{R} E^R + \sum_{R>S} E^{RS}\]

(3)

where (a) \(E^R\) (net energy) contains all energy components internal to the group \(R\), and (b) \(E^{RS}\) (interaction energy) contains the Coulomb interactions between the particles in \(R\) and those in \(S\). The detailed form of these energies is

\[E^R = \langle \Phi_R | \sum_{i \in R} (\hat{T}_i - \sum_{\alpha \in R} Z_\alpha r_{i\alpha}^{-1}) + \frac{1}{2} \sum_{i,j \in R} ' r_{ij}^{-1} | \Phi_R \rangle + \frac{1}{2} \sum_{\alpha, \beta \in R} ' Z_\alpha Z_\beta R_{\alpha\beta}^{-1},\]

(4)

\[E^{RS} = \langle \Phi_R | - \sum_{i \in R} \sum_{\beta \in S} Z_\beta r_{i\beta}^{-1} + \sum_{i \in R} [\hat{V}_c^S(i) + \hat{V}_x^S(i)] | \Phi_R \rangle + \langle \Phi_S | - \sum_{j \in S} \sum_{\alpha \in R} Z_\alpha r_{j\alpha}^{-1} | \Phi_S \rangle + \sum_{\alpha \in R} \sum_{\beta \in S} Z_\alpha Z_\beta R_{\alpha\beta}^{-1},\]

(5)

where \(i, j\) are electrons, \(\alpha, \beta\) nuclei, \(Z_\alpha\) is an atomic number, and \(r_{ij}, r_{i\alpha}\) and \(R_{\alpha\beta}\) are distances between particles.
Let us assume that we are mainly interested in a particular group: the **active group** $A$. All energy components in which $A$ appears can be collected to form the **effective energy** of this group:

$$E_{\text{eff}}^A = E^A + \sum_{R \neq A} E^AR = E_{\text{net}}^A + E_{\text{int}}^A. \quad (6)$$

**Restricted variational principle:** Because $E_{\text{eff}}^A$ is the only part of the total energy that depends on $\Phi_A$, the best group function for the active group can be obtained by minimizing its effective energy while keeping the strong orthogonality with respect to the other, **frozen groups**.

In many instances the frozen groups can be adequately described by single Slater determinants. This is the case for a system of closed-shell frozen groups. The effective energy can then be derived from an effective hamiltonian:

$$E_{\text{eff}}^A = \langle \Phi_A | \hat{H}_{\text{eff}}^A | \Phi_A \rangle, \quad (7)$$

$$\hat{H}_{\text{eff}}^A = \sum_{i \in A} \hat{h}_{\text{eff}}^A + \frac{1}{2} \sum_{i,j \in A} r_{ij}^{-1} + \frac{1}{2} \sum_{\alpha,\beta \in A} Z_\alpha Z_\beta R_{\alpha\beta}^{-1} + \sum_{\alpha \in A} \sum_{S \neq A} Z_\alpha V_{\text{eff}}^S(\vec{R}_\alpha), \quad (8)$$

$$\hat{h}_{\text{eff}}^A = \hat{T}(i) - \sum_{\alpha \in A} Z_\alpha r_{i\alpha}^{-1} + \sum_{S \neq A} [V_{\text{eff}}^S(i) + \hat{P}_S(i)]. \quad (9)$$

Each frozen group contributes an effective potential term, $V_{\text{eff}}^S$, plus a projection operator, $\hat{P}_S$. \hfill (5)
The effective potential due to the frozen group $S$ has nuclear attraction, Coulomb and exchange components:

$$V_{\text{eff}}^{S}(i) = - \sum_{\beta \in S} Z_{\beta} r_{i\beta}^{-1} + \hat{V}_{c}^{S}(i) + \hat{V}_{x}^{S}(i).$$

(10)

The nuclear attraction and Coulomb parts act on all charged particles (nuclei and electrons) of the active group, but the exchange part acts only on the electrons. If $S$ has a closed-shell structure Coulomb and exchange parts become:

$$\hat{V}_{c}^{S}(i) = \sum_{g \in S} 2 \hat{J}_{g}, \quad \hat{V}_{x}^{S}(i) = - \sum_{g \in S} \hat{K}_{g},$$

(11)

where $g$ counts occupied orbitals in $S$. $\hat{J}_{g}$ and $\hat{K}_{g}$ are Coulomb and exchange orbital operators, respectively:

$$\langle \varphi_{i}^{A} | \hat{J}_{g} | \varphi_{j}^{A} \rangle = \langle \varphi_{i}^{A}(1) | \varphi_{g}^{S}(2) | r_{12}^{-1} | \varphi_{j}^{A}(1) | \varphi_{g}^{S}(2) \rangle, \quad \langle \varphi_{i}^{A} | \hat{K}_{g} | \varphi_{j}^{A} \rangle = \langle \varphi_{i}^{A}(1) | \varphi_{g}^{S}(2) | r_{12}^{-1} | \varphi_{g}^{S}(1) | \varphi_{j}^{A}(2) \rangle.$$

$\hat{P}^{S}$ projects the occupied levels of the $S$ frozen group out from the active group wave function. This operator represents the strong orthogonality to the group $S$ in the effective hamiltonian of the active group. For a closed-shell $S$ group

$$\hat{P}^{S}(i) = \sum_{g \in S} | \varphi_{g}^{S} \rangle (-2 \epsilon_{g}^{S}) \langle \varphi_{g}^{S} |,$n

(12)

where $g$ sums over all occupied orbitals of $S$, and $\epsilon_{g}$ is the energy of the $\varphi_{g}$ orbital.
la. The ab initio Perturbed Ion method (aiPI)

The aiPI method is a very simple application of the TES formalism designed to work on highly ionic materials:

- The material is assumed to be formed by ions.
- Every ion forms a weakly correlated electronic group.
- Large STO (Slater Type functions) bases are employed on each ion, but only the STO’s of a given center are retained to build its group function.
- Electrostatic interactions are included through an exact summation of the Madelung series.
- A non-local spectral resolution is used for the exchange operator of each frozen group.
- The method is further simplified by assuming spherical symmetry en each center group function. This is equivalent to assume that the radial part of each STO depends on the angular quantum number $l$ but not on the azimuthal one $m$: $|alm, S⟩ = R_{al}(r_S)Y_{lm}(θ_S, φ_S)$ with $\vec{r}_S = \vec{r} - \vec{R}_S$.
- Correlation energy can be included on each ion using any of several density functionals.
- The aiPI equations, that minimize the effective energy of an ion, are iteratively solved for each different type of ion in the material, until convergence is achieved.
- The total energy of a material can be recovered from the additive energies of the different ions. If $A_a B_b C_c ...$ is the stoichiometric formula of the material:

$$E_{add}^A = E_{net}^A + \frac{1}{2} E_{int}^A \implies E = aE_{add}^A + bE_{add}^B + cE_{add}^C + ...$$ (13)
aiPI example: Equilibrium properties of MgO

Cubic, $Fm\bar{3}m$, $a = 4.210$ Å

<table>
<thead>
<tr>
<th></th>
<th>4a</th>
<th>0</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>4b</td>
<td>$1/2$</td>
<td>$1/2$</td>
<td>$1/2$</td>
</tr>
</tbody>
</table>

PI input:

```
uchf
crystal
title MgO. Experimental geometry.
spg f m -3 m
cell 7.9557 7.9557 7.9557 90.0 90.0 90.0
neq 0.0 0.0 0.0 mg.ion mg.int mg.cint mg.lint
neq 0.5 0.5 0.5 o2.ion o2.int o2.cint o2.lint
endcrystal
end
```

The *.ion files contain the basis set, number of electrons, etc. for each different type of ion.

The cpu time is $\approx 44$ s/100 geometries on a 1.1 GHz Intel PIV.
The aiPI calculation provides $E(V)$, where $E$ is the internal energy if we neglect the zero-point contribution. The equilibrium properties and 0 K equation of state are immediately obtained:

$$\min_a E \to \{a_e, E_e\}, \quad E_{\text{latt}} = E_e - E_{\text{vac}}(\text{Mg}^{+2}) - E_{\text{vac}}(\text{O}^{-1}),$$

$$A = E + TS \approx E, \quad p = -\left( \frac{\partial A}{\partial V} \right)_{T}, \quad B_e = -V \left( \frac{\partial p}{\partial V} \right)_{T} \approx V \left( \frac{\partial^2 E}{\partial V^2} \right).$$

<table>
<thead>
<tr>
<th>Prop.</th>
<th>Unit</th>
<th>aiPI</th>
<th>Exptal.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_e$</td>
<td>Å</td>
<td>4.212</td>
<td>4.210</td>
</tr>
<tr>
<td>$E_{\text{latt}}$</td>
<td>kcal/mol</td>
<td>708</td>
<td>725</td>
</tr>
<tr>
<td>$B_e$</td>
<td>GPa</td>
<td>156</td>
<td>163</td>
</tr>
<tr>
<td>$(dB/dp)_e$</td>
<td>—</td>
<td>3.28</td>
<td>4.13</td>
</tr>
<tr>
<td>$C_p$</td>
<td>J/mol K</td>
<td>38.16</td>
<td>37.89</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>$10^{-6}$ K$^{-1}$</td>
<td>24.8</td>
<td>13.5</td>
</tr>
</tbody>
</table>

Thermal properties ($C_p$ and $\alpha = V^{-1}(\partial V/\partial T)_p$) have been obtained using a quasi-harmonic Debye model, that uses $B(V)$ data to get a Debye temperature as a function of volume [Ref. [10]].
B1-B2 transition in alkali halides

### B1 phase

<table>
<thead>
<tr>
<th>Fm$\bar{3}m$</th>
<th>(a, a, a, 90°, 90°, 90°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$ (4a)</td>
<td>0 0 0</td>
</tr>
<tr>
<td>$X$ (4b)</td>
<td>1/2 1/2 1/2</td>
</tr>
</tbody>
</table>

### Rhombohedral intermediate

<table>
<thead>
<tr>
<th>R$3m$</th>
<th>(a, a, a, α, α, α)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$ (1a)</td>
<td>0 0 0</td>
</tr>
<tr>
<td>$X$ (1b)</td>
<td>1/2 1/2 1/2</td>
</tr>
</tbody>
</table>

### B2 phase

<table>
<thead>
<tr>
<th>Pm$\bar{3}m$</th>
<th>(a, a, a, 90°, 90°, 90°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$ (1a)</td>
<td>0 0 0</td>
</tr>
<tr>
<td>$X$ (1b)</td>
<td>1/2 1/2 1/2</td>
</tr>
</tbody>
</table>

$\alpha \in [60° \text{ (B1)}, 90° \text{ (B2)}]$

(2D Bürgers's mechanism)
Some example results for LiCl:

The phase transition is determined by the Gibbs energy:

\[ G^*(\mathbf{x}; p, T) = E(\mathbf{x}) + pV(\mathbf{x}) + A_{\text{vib}}(\mathbf{x}; T), \]  

(16)

where \( \mathbf{x} \) collects all geometrical degrees of freedom. A quasiharmonic Debye model can be used to estimate \( A_{\text{vib}}(\mathbf{x}; T) \) or we can ignore the term (static calculation).

The B1 and B2 phases will be metastable as far as \( G^*(\mathbf{x}; p, T) \) would remain a local minimum for the \( \mathbf{x}_{B1} \) or \( \mathbf{x}_{B2} \) sites. Of particular concern are the \( c_{ij}^{\text{eff}} \) elastic constants, where

\[ c_{ij}^{\text{eff}} = \frac{1}{V} \frac{\partial G^*}{\partial \varepsilon_i \partial \varepsilon_j} \]  

(17)

and \( \varepsilon_i \) are the Voigt reductions of Lagrange’s deformation parameters \( (\varepsilon_4 = 2\varepsilon_{23}) \).
We can determine a reaction path, \((a, \alpha)\) in Buerger’s mechanism, by minimizing \(G^*(x; p, T)\) for fixed values of \(\alpha\). We can see that the reaction paths have a fixed slope at both the B1 and B2 phases. This can be demonstrated to be a direct consequence of the symmetry properties of the hessian matrix \(H = \nabla \otimes \nabla G^*\) at both sites.
Along with the reaction path we also obtain a reaction energy curve, $G(\alpha)$, that determines both the stability of phases and the kinetics of the phase transition. The B1-B2 transition pressure is $P_{tr} \approx 80$ GPa, but there is a significant energy barrier and thus the transformation will occur with hysteresis.
Hysteresis can be qualitatively studied with the help of a very simple kinetics model:

\[
\frac{dn_{B1}}{dP} = \omega_{B1} e^{-\Delta G_{B1 \rightarrow B2}^\dagger / k_B T} n_{B1} - \omega_{B2} e^{-\Delta G_{B2 \rightarrow B1}^\dagger / k_B T} n_{B2},
\]

where \( n_{B1} \) and \( n_{B2} \) are the concentrations of both phases, \( \Delta G^\dagger \) are the energy barriers (different for the \( B1 \rightarrow B2 \) and \( B2 \rightarrow B1 \) ways except on equilibrium), and the \( \omega_i \) are parameters of this simple model.

Equilibrium transition pressures at 300 K (GPa, experimental values in parenthesis) for the B1-B2 transition in alkali halides.

<table>
<thead>
<tr>
<th>( P_{tr} )</th>
<th>F</th>
<th>Cl</th>
<th>Br</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>252</td>
<td>79</td>
<td>94</td>
<td>113</td>
</tr>
<tr>
<td>Na</td>
<td>12 (23–24)</td>
<td>21 (26–30)</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>K</td>
<td>5.6 (1.73)</td>
<td>2.0 (1.9–2.1)</td>
<td>1.64 (1.77)</td>
<td>2.7 (1.8–1.9)</td>
</tr>
<tr>
<td>Rb</td>
<td>-0.2 (0.9–3.3)</td>
<td>0.3 (0.5)</td>
<td>0.1 (0.45)</td>
<td>0.8 (0.3–0.4)</td>
</tr>
<tr>
<td>Cs</td>
<td>-2.6 (2)</td>
<td>-1.3 (B2)</td>
<td>-1.5 (B2)</td>
<td>-0.7 (B2)</td>
</tr>
</tbody>
</table>

(14)
The aiPI description can be used to produce a pseudopotential that represents frozen ions in any embedding problem. The form of the aiPI operators due to $S$ is

$$
\hat{V}_{\text{aiPI}}^S = \hat{V}_{\text{eff}}^S + \hat{P}^S = -\frac{q^S}{r_{iS}} + V_{nc}^S(r_{iS}) - \hat{V}_x^S + \hat{P}^S, \quad (19)
$$

$$
-\hat{V}_x^S + \hat{P}^S = \sum_l \sum_{m=-l}^l \sum_{a,b} |alm, S\rangle [-A(lab, S) + P(lab, S)] \langle blm, S|, \quad (20)
$$

where $|alm, S\rangle$ is a STO function.

The $\hat{V}_{\text{aiPI}}^S$ operator must be converted into a form able to be used in other electronic structure codes. The ECP form (effective core potential) is accepted in most quantum chemical codes:

$$
\hat{U} = -\frac{q^S}{r_{iS}} + U_L(r) + \sum_{\lambda=0}^{L-1} \sum_{\mu=-\lambda}^{\lambda} |Y_{\lambda\mu}\rangle U_{\lambda-L}(r) \langle Y_{\lambda\mu}| \quad (21)
$$

where $U_l(r)$ is a linear combination of GTO’s (Gaussian Type functions). The conversion from $\hat{V}_{\text{aiPI}}^S$ to $\hat{U}$ involves a delicate fit to pass from a combination of many STO’s to a combination of a few GTO’s. The details can be seen in Ref. [16].
The caPS $U_l(r)$ functions for Mg$^{+2}$ and O$^{-2}$ in MgO are shown in the figures below.

- The $U_l(r)$ functions have very large positive and negative values.
- Notice the use of the $\arctan(rU_l)$ transformation to map the $(-\infty, +\infty)$ range into $[-\pi/2, +\pi/2]$.
- The ripples in the mid-distance range tell the atomic shell structure.
- caPS can be used as an outer embedding component of a cluster-in-the-lattice model to prevent the fugue of electrons from the inner cluster to the outer ionic lattice.
Lanzhou 2005

Ib. Cluster-in-the-lattice calculations

This is a technique for obtaining the electronic structure of defects on ionic materials. The system is divided into:

- A **cluster**, \( C \), of atoms surrounding the defect site. The quantum mechanical calculation corresponds to this region, that contains explicit electrons and basis sets. The size of the cluster dominates the computational effort. \( C \) can be further divided into
  - \( C_1 \), an inner cluster whose geometry will be relaxed to accomodate the defect.
  - \( C_2 \), a electronic buffer formed by atoms that keep their geometry fixed as in the host material.

- The **lattice**, \( L \), is formed by a collection of TES frozen groups. The lattice part close to the cluster can be represented with caPS. The Madelung potential created by the lattice ions is of very large range, but quantum chemical codes do not include the special techniques needed to converge the Madelung series. This can be replaced by a *carefully designed* set of point charges.

\[ \text{Cluster + caPS = Quantum region} \]
Cluster models for $M_{Mg}:MgO$ defect centers. The models for $X_{O}:MgO$ centers are equivalent through an exchange of the Mg and O ions.

<table>
<thead>
<tr>
<th>Ions</th>
<th>position</th>
<th>M-4.1.1</th>
<th>M-6.2.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$1M$</td>
<td>$C_1$</td>
<td>$C_1$</td>
</tr>
<tr>
<td>1</td>
<td>$6O$</td>
<td>$C_1$</td>
<td>$C_1$</td>
</tr>
<tr>
<td>2</td>
<td>$12Mg$</td>
<td>caPS</td>
<td>caPS</td>
</tr>
<tr>
<td>3</td>
<td>$8O$</td>
<td>caPS</td>
<td>caPS</td>
</tr>
<tr>
<td>4</td>
<td>$6Mg$</td>
<td>caPS</td>
<td>$C_2$</td>
</tr>
<tr>
<td>5</td>
<td>$24O$</td>
<td>$\mathcal{L}$</td>
<td>$\mathcal{L}$</td>
</tr>
<tr>
<td>6</td>
<td>$24Mg$</td>
<td>$\mathcal{L}$</td>
<td>$\mathcal{L}$</td>
</tr>
<tr>
<td>7</td>
<td>$12Mg$</td>
<td>$\mathcal{L}$</td>
<td>$\mathcal{L}$</td>
</tr>
<tr>
<td>8</td>
<td>$6O$</td>
<td>$\mathcal{L}$</td>
<td>caPS</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>14</td>
<td>$6Mg$</td>
<td>$\mathcal{L}$</td>
<td>caPS</td>
</tr>
</tbody>
</table>

We will examine two different models. The M-6.2.1 model (image on the right) includes a $C_2$ electronic buffer that is absent in the M-4.1.1 model.
The performance of a model can be checked against the self-embedding consistency test. In other words, a cluster-in-the-lattice model of the pure host lattice should reproduce the geometry of the crystal as faithfully as possible.

The lack of a $C_2$ electronic buffer produces a collapse of the Mg cluster ions towards the lattice region in this $O_O$ self-defect.

Furthermore, the small lattice relaxation observed in the self-embedding test can be used to correct the relaxation of true defect calculations.
| Center | $\Delta R_{\text{relax}}$ (Å) $E_{\text{relax}}$ (eV) $\omega_{a_{1g}}$ (cm$^{-1}$) |
|-------|-----------------|-----------------|
| $\text{Mg}_{\text{Mg}}^+$ | 0.030 | -0.060 | 607 |
| $\text{Al}_{\text{Mg}}^+$ | -0.147 | -0.901 | 638 |
| $\text{Be}_{\text{Mg}}^+$ | -0.041 | -0.006 | 551 |
| $\text{Ca}_{\text{Mg}}^+$ | 0.079 | -1.085 | 700 |
| $\text{Sr}_{\text{Mg}}^+$ | 0.133 | -2.826 | 758 |
| $\text{Ba}_{\text{Mg}}^+$ | 0.193 | -6.734 | 855 |
| $\text{Na}_{\text{Mg}}^{+}$ | 0.145 | -2.191 | 656 |

### Cation site defect:
- **Charge rule**: positive charged defects tend to relax *inwards* and negative ones *outwards*.
- **Impurity size rule**: as the impurity cation radius increases an *outwards* push is added.

| Center | $\Delta R_{\text{relax}}$ (Å) $E_{\text{relax}}$ (eV) $\omega_{a_{1g}}$ (cm$^{-1}$) |
|-------|-----------------|-----------------|
| $\text{O}_{\text{O}}^+$ | -0.006 | -0.005 | 678 |
| $\text{F}^{+2}$ | +0.208 | -5.667 | 763 |
| $\text{F}^+$ | +0.094 | -1.196 | 768 |
| $\text{F}_{\text{O}}^+$ | +0.100 | -1.112 | 686 |
| $\text{F}$ | +0.000 | -0.003 | 597 |
| $\text{S}_{\text{O}}^+$ | +0.093 | -1.193 | 756 |
| $\text{Se}_{\text{O}}^+$ | +0.122 | -2.162 | 761 |
| $\text{N}_{\text{O}}^{+}$ | -0.072 | -0.730 | 688 |

### Anion site defect:
- **Neutral $F$ centers** suffer a negligible relaxation. A strong *outwards* shift occurs when electrons are removed from the $F$ center.
- **Charge rule**: positive defects tend to relax *outwards* and negative ones *inwards*.
- **Impurity size rule**: as the impurity cation radius increases an *outwards* push is added.
II. The Quantum Theory of Atoms in Molecules (AIM)

- The topology of the electron density, $\rho(\vec{r})$, provides a unique partition of real space into atomic basins.

- Basins are separated by zero flux surfaces: $\vec{\nabla} \rho(\vec{r}_s) \cdot \vec{n}(\vec{r}_s) = 0$.

- Each basin contains a single maximum of $\rho(\vec{r})$ that coincides with the nucleus of an atom and it is the source of all $\vec{\nabla} \rho(\vec{r})$ gradient lines.

- The only gradient line crossing a zero flux surface (Inter Atomic Surface or IAS) represents the bond path between the two nuclei that the IAS separates.

$\vec{\nabla} \rho(\vec{r})$ vector field for the C$_2$H$_4$ molecule. Field lines are in red, bond paths in blue, and IAS lines are the thick green lines.
• All the sources and drains of the gradient lines are the critical points $\vec{\nabla}\rho(\vec{r}_c) = \vec{0}$. Those points can be classified according to the eigenvalues of the curvature matrix: $H$ ($H_{\xi\zeta} = \partial^2\rho/\partial\xi\partial\zeta; \xi, \zeta = \{x, y, z\}$). In other words, critical points can be classified according to the dimensions of its attraction and repulsion basins:

<table>
<thead>
<tr>
<th>Type</th>
<th>Where</th>
<th>attrac.</th>
<th>repul.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum</td>
<td>n: nucleus</td>
<td>3D</td>
<td>0D</td>
</tr>
<tr>
<td>Saddle-1</td>
<td>b: bond cp.</td>
<td>2D</td>
<td>1D</td>
</tr>
<tr>
<td>Saddle-2</td>
<td>r: ring cp.</td>
<td>1D</td>
<td>2D</td>
</tr>
<tr>
<td>Minimum</td>
<td>c: cage cp.</td>
<td>0D</td>
<td>3D</td>
</tr>
</tbody>
</table>

• Atomic basins in condensed matter are isomorphic to convex polyhedra: each face is an IAS created by a single bond cp, edges are the attraction basins of ring cp’s, and vertices correspond to minima.

• Topological restrictions: $n - b + r - c = 0$, $n, c \geq 1$, $b, r \geq 3$ per unit cell (Morse relationships); $b + c = r + 2$ for each atomic basin (Euler relationship).
The zero flux surface condition defining the atomic basins guarantees that all quantum mechanical operators are locally well defined, are hermitian, and can be integrated on each basin to produce the atomic contribution to the properties of the whole system. For instance:

- electronic population and fluctuation:
  \[ \langle N \rangle_\Omega = \int_\Omega \rho(\vec{r}) \, d\vec{r}, \quad \sigma^2_N(\Omega) = \langle N^2 \rangle_\Omega - \langle N \rangle_\Omega^2; \]

- multipolar moments:
  \[ N^{lm}_\Omega = \int_\Omega r^l S_{lm}(\theta, \phi) \rho(\vec{r}) \, d\vec{r}; \]

- electron kinetic energy:
  \[ -\hbar^2 \int_\Omega d\vec{r} \left[ \nabla^2 + \nabla^2 \right] \rho^1(\vec{r}'; \vec{r}) = K(\Omega) \]
  \[ = \frac{\hbar}{2m_e} \int_\Omega d\vec{r} \left[ \vec{\nabla}' \cdot \vec{\nabla} \right] \rho^1(\vec{r}'; \vec{r}) = G(\Omega) \]
  \[ -\hbar^2 \int_{S(\Omega)} dS \vec{\nabla} \rho(\vec{r}) \cdot \vec{n}(\vec{r}) = 0 \]

This equation is a consequence of \( \nabla^2 (\Phi^* \Phi) = (\nabla^2 + \nabla^2 + 2 \vec{\nabla}' \cdot \vec{\nabla}) (\Phi^* \Phi) \). Notice that \( K(\Omega) \neq G(\Omega) \) unless \( \Omega \) is delimited by zero flux surfaces.

Basin contributions are strictly additive, \( \langle O \rangle = \sum_\Omega \langle O \rangle_\Omega \), and they can be transferred from one compound to another as far as the shape of the basin do not change much.
Some crystal prototypes

Diamond: shared-shell interactions.
\[
\rho_b = 0.2659 \text{ e/bohr}^3 \\
\nabla^2 \rho_b = -0.9044 \text{ e/bohr}^5 \\
q_C = 0
\]

Li$_2$O: closed-shell bonding.
\[
R_{Li} = 1.402 \text{ bohr} \\
\rho_b = 0.0246 \text{ e/bohr}^3 \\
\nabla^2 \rho_b = +0.2076 \text{ e/bohr}^5 \\
q_{Li} = 0.90 \\
q_O = -1.80
\]

Li: metal with NNM.
\[
\text{2 Li, 12 NNM in the unit cell} \\
\text{Volume: 24% Li, 76% NNM} \\
q: +0.825 \text{ Li, } -0.137 \text{ NNM} \\
\text{Radio: 2.023 Li, 1.293 NNM}
\]

\[
\begin{array}{c|cc}
\text{Li-NNM} & \text{nnm-NNM} \\
\hline
\rho_b & 0.0072 & 0.0075 \\
\nabla^2 \rho_b & 0.00526 & -0.00024 \\
\end{array}
\]
Classification of covalent, ionic and metallic solids

van Arkel-Ketelaar diagram is based on electronegativity: $|\chi_A - \chi_B|$ vs. $\langle \chi_i \rangle$.

Appropriate $\rho$ indices?
- charge transfer: $\langle Q/OS \rangle$,
- flatness: $\rho_{\text{min}}/\rho_{\text{max}}$,
- molecularity: $\mu = (\rho_{\text{max}} - \rho_{\text{min}})/\rho_{\text{max}}$
  (if $\nabla^2 \rho_{\text{max}} \times \nabla^2 \rho_{\text{min}} < 0$ and $\mu = 0$ otherwise).

Figure based on HF-LCAO crystal calculations.
Electron density topology in alkaline metals

- Electron density is very flat: \( f = 96\% \) (Li), 95\% (Na, K), 91\% (Rb), and 88\% (Cs).
- Common tendency towards topological change.
- The topology is labile, at difference from ionic and covalent crystals.
- The many topologies can be classified:
  - \( B_2 \): first and second metal neighbors bonded.
  - \( B_1 \): only first metal neighbors bonded.
  - \( M_L \): non-nuclear maxima (NNM) at the \( M-M \) midpoint.
  - \( M_g \): twin NNM on the \( M-M \) line.
  - \( M_i \): NNM on interstitial positions.
- Topologies follow a common sequence on compression: \( B_2 \to B_1 (\to M) \to B_2 \cdot \cdot \cdot \).
- Li shows NNM on a wide range of geometries.
- Upon small compression Na and K show NNM for a small range of geometries.
- Rb and Cs lack NNM.
- The promolecular model or HF calculations on \( M_2 \) and \( M_4 \) clusters explain the results.
The topology of Li is quite labile
Electron density topology in alkaline metals

-7.55
-7.54
-7.53
-7.52
-7.51
-7.50
-7.49
-7.48
-7.47
-7.46

4  5  6  7  8  9
84
86
88
90
92
94
96
98
100

Total Energy (hartree)

flatness, f (%)
a (bohr)
topologies
M_i
M_L
M_g
B_1
B_2
a_{eq}
Li
Electron density topology in alkaline metals

\[ Q (|e|) \]

\[ V / V_0 (%) \]

\[ a / a_{eq} \]

\[ Q_{Li} \]

\[ Q_{Na} \]

\[ Q_{K} \]

\[ V_{Li} \]

\[ V_{Na} \]

\[ V_{K} \]

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Universal sequence of bonding regimes

• Every couple of atoms follows a universal sequence of bonding regimes which is entirely controlled by the interatomic distance.

\[ R \downarrow: \text{closed valence shell} \rightarrow \text{shared val. shell} \rightarrow (\text{NNM}) \rightarrow \text{closed inner shell} \ldots \]

• This sequence is caused by the intrinsic electronic shell structure of atoms, which is largely conserved in general compounds.

• Diatomic molecules serve well to predict the behavior of a bonding pair of atoms in a larger molecular or cristalline environment.

• The promolecular model and, to a lesser extent, its exponential tails simplification provide specific predictions for the bond CP electron density and Laplacian, that agree qualitatively and explain the trends actually observed on state-of-the-art quantum mechanical calculations.

(Ex.) At the \( A-A \) midpoint:

\[
\rho_{\parallel}'' = 2\rho_A''(r_A), \quad \rho_{\perp}'' = 2\rho_A'(r_A)/r_A, \quad \nabla^2 \rho = 2\rho_A''(r_A) + 4\rho_A'(r_A)/r_A
\]
The diagram illustrates the universal sequence of bonding regimes for molecular systems. The figure shows the behavior of the Laplacian of the electron density, $\nabla^2 \rho_b$, as a function of the distance $d$ (in bohr). The graph compares different theoretical methods: Promolecular, HF, CISD, and DFT-BPW91.

- Promolecular: Red solid line
- HF: Green dashed line
- CISD: Blue dotted line
- DFT-BPW91: Pink dash-dotted line

The graph highlights the regions where $\nabla^2 \rho_b > 0$ and $\nabla^2 \rho_b < 0$, indicating different bonding regimes. The inset focuses on the behavior at smaller distances.
fpLAPW/GGA (**WIEN**): diamond, graphite, CaC₂.

B3LYP/6-311G(3df,p) (**GAUSSIAN**): C₂, ethane, ethylene, acetylene, benzene, anthracene, alene.

\[ \nabla^2 \rho_b < 0 \quad \nabla^2 \rho_b > 0 \n\]

\[ C_2 \left( ^3 \Pi_u \right) \]

\[ \text{interatomic distance, } d \text{ (bohr)} \]

\[ \text{bond density, } \rho_b \text{ (e/bohr}^3) \]

\[ \text{NNM} \]
Partition of thermodynamical properties

- The partition of atomic compressibility is simple:

\[
\kappa = \frac{1}{B} = -\frac{1}{\Omega} \left( \frac{\partial \Omega}{\partial p} \right), \quad \Omega = \sum_i \Omega_i, \quad f_i = \frac{\Omega_i}{\Omega},
\]

\[
\kappa_i = \frac{1}{B_i} = -\frac{1}{\Omega_i} \left( \frac{\partial \Omega_i}{\partial p} \right) \quad \Rightarrow \quad \kappa = \sum_i f_i \kappa_i.
\]

- This provides a very practical analytical tool. A well known *rule of thumb* says that oxide spinels have a bulk modulus of \(\approx 200\) GPa. Why?

<table>
<thead>
<tr>
<th>$AB_2O_4$</th>
<th>$B$ (GPa)</th>
<th>$B_A$</th>
<th>$B_B$</th>
<th>$B_O$</th>
<th>$f_O$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgAl$_2$O$_4$</td>
<td>215.2</td>
<td>282.1</td>
<td>331.9</td>
<td>201.6</td>
<td>0.8127</td>
</tr>
<tr>
<td>MgGa$_2$O$_4$</td>
<td>211.2</td>
<td>261.2</td>
<td>283.9</td>
<td>196.1</td>
<td>0.7486</td>
</tr>
<tr>
<td>ZnAl$_2$O$_4$</td>
<td>214.8</td>
<td>246.0</td>
<td>335.2</td>
<td>203.3</td>
<td>0.7690</td>
</tr>
<tr>
<td>ZnGa$_2$O$_4$</td>
<td>213.3</td>
<td>241.2</td>
<td>308.6</td>
<td>195.7</td>
<td>0.7070</td>
</tr>
</tbody>
</table>

Most of the crystal volume is occupied by the oxide ion. Therefore \(\kappa \approx \kappa_O\).

- This has geophysical consequences, as most crust and mantle minerals are oxide-rich. Is the average compressibility of Earth mantle dominated by \(\kappa_O(p, T)\)?
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References