How to model Solids?

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- Crystals are periodic, $\Psi(\pmb{x} + \pmb{R}) = \Psi(\pmb{x})$
- k-points
- A simple hint: think about the size of Hamiltonian, Density Matrix, etc.
- H_{ab}(k) ==>H_{AB}(0), so for a supercell 2x2x2 is equivalent of 8 k-points. So, if we have a molecule in a unit cell with 10 basis functions, we will have 80 BF for the supercell.
- Periodicity has a drawback: all defects are periodic (including charged), all excitations are also periodic.
- as a result: many periodic codes with HF and DFT.
- local MP2, local CCSD, etc.

- Main advantage: all molecular codes are compatible with the cluster model
- Main disadvantage: significant border effects, any calculation needs thinking and complicated setup
- Larger cluster means even larger amount of border atoms
- Different strategies for ionic systems and for covalent systems
- What is wrong with QM/MM?

- PCM-like model for bio-organic systems
- Mixing of different basis sets
- Covalent bonds are strong and directed
- Termination by H-atoms
- Ideal solution: a mono valent hydrogen atom with a size (and electronegativity) of carbon / silicon etc.
- Artificial model potentials

- Reference: a periodic calculation. Charges are \pm 1.48.
- With increase of clusters the central part becomes similar to periodic. With point charges the convergence is faster.
- The "buffer" atoms near the border are expensive: they are in large numbers and they have basis set functions
- A layer between Quantum part and charges is also needed.

	Mg ₄ O ₄		[MgO	$6]^{-10}$	$[OMg_{6}]^{+10}$		$[MgO_6Mg_{18}]^{+26}$		$[OMg_6O_{18}]^{-26}$	
BC	+1.18	-1.18	-0.42	-1.60	+1.95	-1.67	+1.33	-1.67	+1.52	-1.55
PC	+1.71	-1.71	+1.39	-1.90	+1.93	-1.60	+1.36	-1.56	+1.45	-1.55

AIMPS

- Group Function Theory McWeeny, R. ReV. Mod. Phys. 1960, 32, 335.
- Huzinaga Cantu equation Huzinaga, S.; Cantu, A. A. J. Chem. Phys. 1971, 55, 5543.



stem is partitioned into weekly interacting electronic groups

R. McWeeny Rev. Mod. Phys. 32 (1960) 335

The whole system wave function Φ_{κ} is an antisymmetric product

$$\Phi_{\kappa} = M_{\kappa} \hat{A} \left[\Phi_r^R \Phi_s^S \dots \right] \quad (\kappa = Rr, Ss, \dots).$$

 R, S, \ldots denotes electronics groups, whose electronic states r, s, \ldots are represented by $\Phi_r^R, \Phi_s^S \ldots$ antisymmetric group functions of N_R, N_S, \ldots electrons respectively. M_κ normalization factor \hat{A} the inter group antisymmetrizer

The group functions should fulfil strong orthogonality conditions

$$\int \Phi_r^R(x_1, x_2, \dots, x_i, x_j, \dots) \Phi_s^S(x_1, x_2, \dots, x_k, x_l, \dots) dx_1 = 0$$

for $R \neq S$

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for $R \neq S$

Orbital sets!

The condition can be achieved if Φ_r^R and Φ_s^S are constructed with different and orthogonal spin-orbital sets.

If strong orthogonality condition is fulfilled then the energy associated with the total wave function is partitioned as

$$E = \sum_{R} H^{R}(rr) + \sum_{R < S} \left[J^{RS}(rr, ss) - K^{RS}(rr, ss) \right].$$

The following terms

$$E_{eff}^{R} = H^{R}(rr) + \sum_{S(
eq R)} \left[J^{RS}(rr, ss) - K^{RS}(rr, ss)
ight]$$

stand for the energy of R electronic group under the interactions with the other electron groups.

Modified sum of one electron Hamiltonian R

$$\hat{h}_{eff}^{R} = \sum_{i=1}^{N_{R}} \left\{ -\frac{1}{2} \nabla_{i}^{2} - \sum_{\mu} \frac{Z_{\mu}}{|\boldsymbol{r}_{i} - \boldsymbol{R}_{\mu}|} + \sum_{\boldsymbol{S} \neq \boldsymbol{R}} \left[\hat{J}^{\boldsymbol{S}}(i) - \hat{K}^{\boldsymbol{S}}(i, i') \right] \right\}$$

The operators $\hat{J}^{S}(i)$ and $\hat{K}^{S}(i, i')$ are the Coulomb and exchange operators for an electron in the effective field due to the electrons of group S.

Embedded cluster approach



Ernst D. Larsson, Marek Krośnicki, Valera Veryazov, A program system for self-consistent embedded potentials for ionic crystals, Chemical Physics, **562** (2022) 111549 G. L. Manni et al *The OpenMolcas Web: A Community-Driven Approach to Advancing Computational Chemistry* J. Chem. Theory Comput. **19** (2023) 6933–6991 Hartree-Fock equation:

$$\hat{f} \ket{\psi_i} = \epsilon_i \ket{\psi_i}$$

in AIMP the Fock operator, $\hat{f},$ is replaced by

$$\hat{f}^{AIMP} = \hat{f} - 2\sum_{k} \epsilon_{k} \ket{\psi_{k}} \langle \psi_{k} |.$$

For details see:

L. Seijo and Z. Barandiarán, The ab initio model potential method: A common strategy for effective core potential and embedded cluster calculations, in Computational Chemistry: Reviews of Current Trends, Vol. 4, edited by J. Leszczynski, (Wold Scientific, Singapur, 1999), pp. 55-152.

Representation of core potentials

$$\begin{split} \hat{V}_{coul}^{AIMP}(r) &= \frac{\sum_{k} c_{k} e^{-\alpha_{k} r^{2}}}{r}, \\ \hat{V}_{exch}^{AIMP} &= \sum_{l} \sum_{m=-l}^{l} \sum_{ab} \left| \psi_{alm} \right\rangle A_{l;ab} \left\langle \psi_{blm} \right|, \end{split}$$

where $|\psi_{alm}\rangle = |\phi_a\rangle |\vartheta(l,m)\rangle$; $|\phi_a\rangle$ corresponds to the radial primitive basis and $|\vartheta(l,m)\rangle$ the spherical harmonics. $A_{l;ab}$ is related to the exact exchange operator, \hat{V}_{exch} , via

$$\mathsf{A} = \mathsf{S}^{-1}\mathsf{K}\mathsf{S}^{-1},\tag{1}$$

Flow chart

SCEPIC: https://gitlab.com/ErnDLar/scepic



Input: extended (MOLCAS) XYZ formatted file. Extra - atomic exponents and Hamiltonian (to compute an ion in a crystal environment). Output: ready to use library Larsson et al. Chem. Phys **562** (2022) 111549 Manni et al. J. Chem. Theory Comput. **19** (2023) 6933–6991 From left to right: MgO cluster with basis (note that basis set for outer atoms can be very small), layer of AIMPs (picture was zoomed out): quantum part is well separated, point charges (again zoomed out): neutral, no dipole (multiple) moments



- One-electron approach: HOMO-LUMO gap
- This is the only possible solution for periodic calculations All data is in eV.

crystal	MgO	CaO	CaF_2
Periodic (PBE)	4.1	3.7	6.4
Cluster (PBE)	4.9	3.9	8.0
Experiment	7.8	7.1	11.2

• Calculation of states: ground and excited

crystal	MgO	CaO	CaF_2
Periodic (PBE)	4.1	3.7	6.4
Cluster (PBE)	4.9	3.9	8.0
Cluster (MS-CASPT2)	7.6	5.5	10.8
Experiment	7.8	7.1	11.2

MS-CASPT2 calculations are better, but still far from ideal: small cluster size, small active space. Also note that cluster model needs much larger sizes to model non-direct gaps.

Band gaps computed with the $[MgO_6Mg_{18}]^{26+}$, $[CaO_6Ca_{18}]^{26+}$ and $[CaF_8Ca_{12}]^{18+}$ -clusters using various embedding methods. MS-CASPT2 calculations were for the four lowest roots of a (12e,10o)-active space for MgO and CaO. For CaF₂, a (16e,12o) active space was used.

Local properties of the density matrix

- Based on the Population Matrix P = DS, or transformed, e.g. by Löwdin orthogonalization
- Properties of Population Matrix
 - idempotent $P^2 = 2 * P$
 - $\sum P_{ii} = N$
 - $\sum P_{ij} * P_{ji} = ?$ (use idempotency to solve)
- selection of 'atomic' blocks
 - electronic charge $N_A = \sum_{i \in A} P_{ii}$
 - bond order $W_{AB} = \sum_{i \in A, j \in B} |P_{ij}|^2$
 - covalency $C_A = \sum_{A \neq B} W_{AB}$
 - full valency $V_A = rac{1}{2}C_A + |Q_A|$ or $rac{1}{2}\sqrt{C_A^2 + 4Q_A^2}$
- A convenient way to describe electronic structure, especially in solids, many of them have a mixture of covalent and ionic bonds

Valency

R. A. Evarestov and V. A. Veryazov "Quantum-chemical definition of the atomic valence in molecules and crystals", Theor. Chem. Acc. 81, pages 95-103, (1991)

$$V_{A} = \frac{\left(C_{A} + (C_{A}^{2} + 4Q_{A}^{2})^{1/2}\right)}{2}$$

How it works. VV did an example calculations for ThF systems (ThF_n (n=1,2,3,4)), ANO-RCC-VTZP, 12 active orbitals

		Th	F	F	F	F
ThF ₁	Charge	0.6927	-0.6927			
	Valence	1.1431	1.1431			
ThF ₂	Charge	1.3744	-0.6749	-0.6994		
	Valence	2.2331	1.1341	1.1432		
ThF ₃	Charge	2.0773	-0.6533	-0.7121	-0.7119	
	Valence	3.1762	1.0666	1.0862	1.0864	
ThF ₄	Charge	2.8240	-0.7097	-0.7086	-0.7086	-0.6971
	Valence	4.1239	1.0679	1.0670	1.0671	1.0621

Cluster	Site	Valency	Excitation
			Energy, eV
$[ThF_6Ca_{12}]^{+22}$	double F^- vacancy	4.18	6.19
$[ThF_7Ca_{12}]^{+21}$	single F^- vacancy	2.20	8.03
$[ThF_8Ca_{11}]^{+18}$	Ca ⁺² vacancy	4.21	9.72
$[ThF_8Ca_{12}]^{+20}$	8 F ⁻ coordinated Th(IV)	4.22	10.28
$[ThF_{10}Ca_{12}]^{+18}$	10 F ⁻ coordinated Th(IV)	4.21	11.34

Ce:YVO4 (JCP 159, 114117 (2023)) - Th:CaF2 (Phys. Rev. B 111, 115103 (2025))



Solids need more attention (long range Coulomb, broken bonds on the edges) and more computational resources, but all methods you learned here can be applied to cluster model of solids.

lonic systems - Intro into exercises



- LiF crystal has FCC structure. How to model it by a cluster?
- Stoichiometric cluster must be too big to ensure proper surrounding even in the central part of the cluster
- Which of LiF_6 and FLi_6 is better?
- Think which border atom is more compact?
- Think which basis size is smaller?
- For non stoichiometric clusters we need to specify the number of electrons..

- we can set up any charge, and investigate Energy as a function of Q (e.g. at HF level).
- $\bullet\,$ For ${\sf FLi_6}^{+Q}$ cluster the minimum energy corresponds to $Q{=}{+1}$
- If we add some negative charges around the minimum will be at Q=+4 .. +6
- Bare clusters are not good.
- Adding point charges solves the problem only partially, since the attraction (or repulsion) between charges and electrons is too high