A brief introduction to computational aspects of quantum chemistry

E.Giner

Laboratoire de chimie théorique, Paris

1 The specificity of the quantum chemistry problem

- 2 Back to basics: the basis set
- Typical scaling of WFT methods

What is a chemical system ?

• Which atoms and where are they: {*Z_k*, **R**_{*k*}} Example: H₂O at equilibrium geometry



Inp	ut	file for	H2O at R_e	q (Angstroms)
Н	1	0.751	0.194	0.000
0	8	0.000	-0.388	0.000
Н	1	-0.751	0.194	0.000

- Total charge: number of electrons N_e Example: H₂O has 10 electrons Example: (H₂O)⁺ has 9 electrons
- What is interesting for a chemist
 - Energy differences obtained by varying N_e and $\{Z_k, \mathbf{R}_k\}$

The electronic structure of a molecule

 N_e and $\{Z_k, \mathbf{R}_k\}$ are known \Rightarrow the BO Hamiltonian is known

$$\hat{H}(N_e, \{\mathbf{R}_k, Z_k\}) = \sum_{i=1}^{N_e} \left(\underbrace{-\frac{1}{2} \Delta_i + \sum_{j>i} \frac{1}{r_{ij}}}_{\text{universal for } N_e} + \underbrace{v_{ne}(\mathbf{r}_i, \{\mathbf{R}_k, Z_k\})}_{\text{system specific}} \right) + \sum_{k,l} \frac{Z_k Z_l}{|\mathbf{R}_k - \mathbf{R}_l|}$$
$$v_{ne}(\mathbf{r}_i, \{\mathbf{R}_k, Z_k\}) = -\sum_{k=1}^{N_{\text{nucl}}} \frac{Z_k}{|\mathbf{r}_i - \mathbf{R}_k|}$$

One needs to solve the Schrodinger equation for a state i

$$\hat{H}(N_e, \{\mathbf{R}_k, Z_k\}) |\Psi_i\rangle = E_i(N_e, \{\mathbf{R}_k, Z_k\}) |\Psi_i\rangle$$

 $|\Psi_i\rangle = |\Psi_i(N_e, \{\mathbf{R}_k, Z_k\})\rangle$

 $\{\mathbf{R}_k, Z_k\}$ and N_e are parameters

- Changing $\{\mathbf{R}_k\}$ and/or Z_k is equivalent to change \hat{H}
- It creates a one body attractive field for electrons
- The density is concentrated around the nuclei

Globally v_{ne} is larger W_{ee}

Globally v_{ne} is larger W_{ee}

Electrons are **bound** near the nuclei

• Large energy splitting between levels

Globally v_{ne} is larger W_{ee}

- Large energy splitting between levels
 - The shell model makes sense \Leftrightarrow mean-field approaches
 - Notion of "core" and "valence" electrons
 - Most of the molecules exist at HF level
 - Non mean-field part of W_{ee} is small (0.1 % of the Energy)

Globally v_{ne} is larger W_{ee}

- Large energy splitting between levels
 - The shell model makes sense \Leftrightarrow mean-field approaches
 - Notion of "core" and "valence" electrons
 - Most of the molecules exist at HF level
 - Non mean-field part of W_{ee} is small (0.1 % of the Energy)
- Atomic orbitals as a basis set (see next)

Globally v_{ne} is larger W_{ee}

- Large energy splitting between levels
 - The shell model makes sense \Leftrightarrow mean-field approaches
 - Notion of "core" and "valence" electrons
 - Most of the molecules exist at HF level
 - Non mean-field part of W_{ee} is small (0.1 % of the Energy)
- Atomic orbitals as a basis set (see next)
 - In practice use polynoms × gaussians

$$\chi_{i}^{J}(\mathbf{r}) = (x - X_{J})^{a_{x}} (y - Y_{J})^{a_{y}} (z - Z_{J})^{a_{z}} e^{-\alpha_{i}(\mathbf{r} - \mathbf{R}_{J})^{2}}$$

Globally v_{ne} is larger W_{ee}

- Large energy splitting between levels
 - The shell model makes sense \Leftrightarrow mean-field approaches
 - Notion of "core" and "valence" electrons
 - Most of the molecules exist at HF level
 - Non mean-field part of W_{ee} is small (0.1 % of the Energy)
- Atomic orbitals as a basis set (see next)
 - In practice use polynoms × gaussians

$$\chi_{i}^{J}(\mathbf{r}) = (x - X_{J})^{a_{x}} (y - Y_{J})^{a_{y}} (z - Z_{J})^{a_{z}} e^{-\alpha_{i}(\mathbf{r} - \mathbf{R}_{J})^{2}}$$

- All Hamiltonian integrals are analytical in that basis
- "Easy" to refine the basis set (e.g degree of polynoms)

Ability of **unraveling chemistry** \Leftrightarrow **Accuracy of** ΔE

Ability of **unraveling chemistry** \Leftrightarrow **Accuracy of** ΔE

The famous chemical accuracy in quantum chemistry

- "Chemical accuracy" $\approx 1 \mbox{ kcal/mol} \approx 1.6 \ 10^{-3} \mbox{ a.u.} \approx 0.04 \ eV$
 - accuracy of thermochemistry experiments
 - $\bullet~\approx 0.2$ of Bolzman probability ratio at 298 K

Ability of **unraveling chemistry** \Leftrightarrow **Accuracy of** $\triangle E$

The famous **chemical accuracy** in quantum chemistry

- "Chemical accuracy" $\approx 1 \mbox{ kcal/mol} \approx 1.6 \ 10^{-3} \mbox{ a.u.} \approx 0.04 \ eV$
 - accuracy of thermochemistry experiments
 - $\bullet~\approx 0.2$ of Bolzman probability ratio at 298 K
- Typical quantity of interest: atomization energy (AE)

$$\mathsf{AE}(AB) = \mathsf{E}(AB) - (\mathsf{E}(A) + \mathsf{E}(B))$$

- $10^0 < AE < 10^2 \text{ kcal/mol}$
- Typical error at HF level: $\approx 10^1 \text{ or even} \approx 10^2 \text{ kcal/mol}$

Ability of **unraveling chemistry** \Leftrightarrow **Accuracy of** $\triangle E$

The famous **chemical accuracy** in quantum chemistry

- "Chemical accuracy" $\approx 1 \mbox{ kcal/mol} \approx 1.6 \ 10^{-3} \mbox{ a.u.} \approx 0.04 \ eV$
 - accuracy of thermochemistry experiments
 - $\bullet~\approx 0.2$ of Bolzman probability ratio at 298 K
- Typical quantity of interest: atomization energy (AE)

$$\mathsf{AE}(AB) = \mathsf{E}(AB) - (\mathsf{E}(A) + \mathsf{E}(B))$$

- $10^0 < AE < 10^2 \text{ kcal/mol}$
- Typical error at HF level: $\approx 10^1 \text{ or even} \approx 10^2 \text{ kcal/mol}$

What do we miss ? The correlation effects !

What tools for correlation ?

Two types of approaches

• Density Functiona Theory (DFT)

- Uses the 1-body density and its derivatives: very cheap !
- Until the last years, clearly the most used tool
- BUT: Problems with non-local correlation effects ...
- BUT: Hard to systematically improve the quality
- Alternative: mixing WFT and DFT ?

• Wave Function Theory (WFT)

- Uses the *N*-body wave function: not cheap ...
- Until recently, much less used than DFT ...
- Systematically improvable
- CC very reliable for most of chemical situation
- BUT: strong scaling with system size $\propto N^5, N^6, \cdots$
- Need of large basis sets to achieve accuracy
- BUT: exploit locality (PNOs) and explicit correlation (F12)

Quantum chemistry from outside: why so many acronyms

(Some) Acronyms for Wave Function Theory ...

- HF, MP2, CEPA-n, CISD(SC)², CCSD(T), BCCD(T), EOM-CCSD(T), PNO-CCSD(T), DLPNO-CCSD(T), ...
- CASCI, CASSCF, MCSCF, MRMP2, XMCQDPT, CASPT2, MS-CASPT2, NEVPT2, SC-NEVPT2, PC-NEVPT2, QD-NEVPT2, JMMRPT2, ...
- CIPSI, HBCI, MPS, DMRG, FCIQMC, *i*FCIQMC, ACI, SORCI, DDCI, FOBOCI, ...
- SS-MRCC, SU-MRCC, VU-MRCC, JM-MRCC, Mk-MRCCSDT, ic-MRCC, ...
- F12-MP2, F12-CCSD(T), F12-NEVPT2, F12-DLPNO-NEVPT2, RS-DFT, ...

Quantum chemistry from outside: why so many acronyms

(Some) Density Functional Theory acronyms ... wB97 X3LYP PW92 BNL05 **PW91** OBPW M06-L WC06 wB97XD LB9483 VP86 PBESO wB97X B2PLYF BMK04 BOP FT97 **B97** PBEOP CSI rB86 Bh3LYP GV09 105-2X HSE BR89 muB88 HL71 **XPBE** M06-H M06-2X revPRF HCTH PKZB99 muPBE LRC-wPBE0 LG93 KCIS wigner **O3LYF** LC-wPB PKO6 B EDF1 B86-mgc VS98 B94 AM PW86 B97-1 EDF2 mPBE KT3 VWNI WPBE

Molecular simulations: why so many acronyms ?

Mainly two answers ...

- Quantum chemists have a bigger ego issue
 - The researcher ego is quite uniformly distributed in science

Molecular simulations: why so many acronyms ?

Mainly two answers ...

- Quantum chemists have a bigger ego issue
 - The researcher ego is quite uniformly distributed in science
- ② The theoretical chemistry problem is very heterogeneous

Molecular simulations: why so many acronyms ?

Mainly two answers ...

- Quantum chemists have a bigger ego issue
 - The researcher ego is quite uniformly distributed in science
- **2** The theoretical chemistry problem is very **heterogeneous**

The main objectives of molecular simulation

- Predict and/or interpret molecular experiments
- Basically infinite possibilities at human scale !

Molecular simulation is as diverse as chemistry can be !

An overview of the heterogeneity of theoretical chemistry

Two main variables to define a chemistry experiment

- Types of molecular properties
 ⇒ Different objects to compute
- Types of molecular systems
 - \Rightarrow Different size of systems
 - \Rightarrow Different level of *e*-*e* correlation

Different implications for the theoretician

A few examples of molecular properties

Different chemical problematics

- Formation of molecules
 - Gd state energy
 - Energy derivatives with ${\boldsymbol{\mathsf{R}}}$
- UV/visible spectroscopy
 - Excited states
 - Oscillation strength
- Magnetic spectroscopy
 - Open shell systems
 - Energy derivatives with **B**
- Any combination ...



- Size of the system
 - from 10^0 to 10^2 electrons



- Size of the system
 - from 10^0 to 10^2 electrons



- Size of the system
 - $\bullet~from~10^0$ to $10^2~electrons$
- Elements in the systems

- Size of the system
 - from 10^0 to 10^2 electrons
- Elements in the systems
 - s or p atoms (H, C, N,..): "Easy" atoms

н																-	2 He
Li	Be											5 в	°c	7 N	o	F	¹⁰ Ne
Na	12 Mg											13 A	14 Si	15 P	16 S	17 CI	18 Ar
ĸ	Ca	Sc	22 Ti	v	Cr	a Mn	Fe	Co	28 Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	Ru	Rh	⁶⁶ Pd	47 Ag	Cd	a) In	S0 Sn	51 Sb	52 Te	53 I	54 Xe
Cs	50 Ba	ĺ.	72 Hf	Ta	24 W	75 Re	76 Os	; ⁷⁷ Ir	78 Pt	79 Au	Hg	81 TI	Pb	Bi	Po	as At	86 Rn
Fr	Ra	*	104 Rf	Db	Sg	107 Bh	108 Hs	109 Mt	110 Ds	Rg	Uul	b 113 Uu	t Uuc	115 Uup	Uuh	Uus	118 Uuo
* Lanti Ser	hanide ies	57 La	58 Ce	59 Pr	50 Nd	Pm	62 Sm	63 Eu	64 Gd	65 Tb	55 Dy	67 Ho	68 Er	⁶⁹ Tm	70 Yb	Lu	
+ Actinide Series		Ac	90 Th	Pa	92 U	23 Np	Pu	95 Am	⁹⁶ Cm	97 Bk	Cf	en Es	100 Fm	¹⁰¹ Md	102 No	Lr	
Alkali r	votala	Alkalin	e earth tals	Lanthan	side	Actinoide		metals	Poor	metals	Metal	loids	Other		Halogens	Nobi	e Gases

A few examples of molecular systems

Different types of systems

- Size of the system
 - from 10^0 to 10^2 electrons

• Elements in the systems

 s or p atoms (H, C, N,..): "Easy" atoms



A few examples of molecular systems

Different types of systems

- Size of the system
 - from 10^0 to 10^2 electrons

• Elements in the systems

- s or p atoms (H, C, N,..): "Easy" atoms
- *d* or *f* atoms (Fe, Dy, ..): "Hard" atoms

ĥ]																	He
Li	Be												5 B	°c	⁷ N	o	F	¹⁰ Ne
Na	12 Mg												"AI	14 Si	15 P	10 S	17 CI	18 Ar
¹⁹ K	20 C	,	21 Sc	22 Ti	23 V	Cr	25 Mn	Fe	Co	28 Ni	29 Cu	DO Zn	Ga	32 Ge	an As	34 Se	35 Br	» Kr
37 Rb	38 S	1	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	ei Ru	45 Rh	⁴⁶ Pd	47 Ag	48 Cd	ey. In	so Sn	51 Sb	52 Te	53 I	54 Xe
SS Cs	50 B	Ī	•	72 Hf	73 Ta	24 W	75 Re	⁷⁶ Os	"Ir	78 Pt	79 Au	eo Hg	81. 71	Pb	Bi	Po	as At	86 Rn
e7 Fr	no R		*	104 Rf	Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	Rg	Uub	Uut	114 Uuq	115 Uup	Uuh	Uus	118 Uuo
* Lanti Ser	hanide ies	50	La	Se Ce	⁵⁹ Pr	® Nd	oi Pm	Sm	63 Eu	64 Gd	⁶⁵ ТЬ	* Dy	67 Ho	Er	Tm	УЪ	Lu	
+ Act Ser	inide les	55	Ac	^{so} Th	Pa	92 U	²³ Np	Pu	Am	⁹⁶ Cm	97 Bk	⁹⁸ Cf	20 Es	Fm	Md	No	Lr	
Alkali r	vetala	ľ	meta	earth ris	Lanthano	da .	Actinoide	1	ensition netels	Peer	metals	Metalli	xida	Other Norwneta	. "	lalogens	Nobi	Gases

A few examples of molecular systems

Different types of systems

- Size of the system
 - from 10^0 to 10^2 electrons

• Elements in the systems

- s or p atoms (H, C, N,..): "Easy" atoms
- d or f atoms (Fe, Dy, ..): "Hard" atoms



A few examples of molecular systems

Different types of systems

- Size of the system
 - from 10^0 to 10^2 electrons

• Elements in the systems

- s or p atoms (H, C, N,..): "Easy" atoms
- d or f atoms (Fe, Dy, ..): "Hard" atoms

• Electronic structure

- Are there unpaired electrons ?
- Is HF a good representation ?



Brief conclusion

- A LOT of different methods in QC
 - ⇒ MANY different chemical situations
- Strong constraints:
 - accuracy of ΔE (the famous kcal/mol)
 - size of the system (from 10 to 1000)
 - strength of correlation in the system
- Current status
 - Weak correlation is on the way to be solved:
 ⇒ CC hierarchy, local approaches and F12
 - Strong correlation is still an open question:
 ⇒ struggle between many approaches

The guide towards quantum chemistry calculations

- The symmetries of the Hamiltonian
- Obfine the Hamiltonian in second quantized form
- What kind of integrals we need to evaluate ?
- What basis set do we use ?
 - How we build it ?
 - What are the constraints ?
- Typical quantum chemistry correlated WFT calculations
 - What is the impact of the basis set ?
 - How the energy differences converge with the basis set ?
 - What is the effect of correlation ?

The Hamiltonian

 N_e and $\{Z_k, \mathbf{R}_k\}$ are known \Rightarrow the BO Hamiltonian is known

$$\hat{H}(N_{e}, \{\mathbf{R}_{k}, Z_{k}\}) = \sum_{i=1}^{N_{e}} \left(\underbrace{-\frac{1}{2} \Delta_{i} + \sum_{j > i} \frac{1}{r_{ij}}}_{\text{universal for } N_{e}} + \underbrace{\underbrace{v_{ne}(\mathbf{r}_{i}, \{\mathbf{R}_{k}, Z_{k}\})}_{\text{system specific}} \right) + \sum_{k,l} \frac{Z_{k} Z_{l}}{|\mathbf{R}_{k} - \mathbf{R}_{l}|}$$

$$v_{ne}(\mathbf{r}_{i}, \{\mathbf{R}_{k}, Z_{k}\}) = -\sum_{k=1}^{N_{nucl}} \frac{Z_{k}}{|\mathbf{r}_{i} - \mathbf{R}_{k}|}$$

The symmetries of the chemical BO Hamiltonian

• Number of particles: $[\hat{H}, \hat{N}] = 0$ $\Rightarrow N_e$ is constant

The symmetries of the chemical BO Hamiltonian

- Number of particles: $[\hat{H}, \hat{N}] = 0$
 - $\Rightarrow N_e$ is constant
- Total spin S^2 : $[\hat{H}, \hat{S}^2] = 0$
 - \Rightarrow Work within a given eigenvalue of \hat{S}^2

The symmetries of the chemical BO Hamiltonian

- Number of particles: $[\hat{H}, \hat{N}] = 0$
 - $\Rightarrow N_e$ is constant
- Total spin S^2 : $[\hat{H}, \hat{S}^2] = 0$ \Rightarrow Work within a given eigenvalue of \hat{S}^2
- Spin projection on z: $[\hat{H}, \hat{S}_z] = 0$
 - ⇒ Defines $(n_{\alpha}, n_{\beta}) \Leftrightarrow (n_{\uparrow}, n_{\downarrow})$ compatible with the $\langle \hat{S}^2 \rangle$ value ⇒ $N_e = n_{\alpha} + n_{\beta}$
- Number of particles: $[\hat{H}, \hat{N}] = 0$
 - $\Rightarrow N_e$ is constant
- Total spin S²: [Ĥ, Ŝ²] = 0
 ⇒ Work within a given eigenvalue of Ŝ²
- Spin projection on z: $[\hat{H}, \hat{S}_z] = 0$
 - ⇒ Defines $(n_{\alpha}, n_{\beta}) \Leftrightarrow (n_{\uparrow}, n_{\downarrow})$ compatible with the $\langle \hat{S}^2 \rangle$ value ⇒ $N_e = n_{\alpha} + n_{\beta}$

• H₂O : $N_e = 10$ in a singlet state $\langle \hat{S}^2 \rangle = 0 \Rightarrow n_\alpha = n_\beta = 5$

- Number of particles: $[\hat{H}, \hat{N}] = 0$
 - $\Rightarrow N_e$ is constant
- Total spin S²: [Ĥ, Ŝ²] = 0
 ⇒ Work within a given eigenvalue of Ŝ²
- Spin projection on z: $[\hat{H}, \hat{S}_z] = 0$
 - ⇒ Defines $(n_{\alpha}, n_{\beta}) \Leftrightarrow (n_{\uparrow}, n_{\downarrow})$ compatible with the $\langle \hat{S}^2 \rangle$ value ⇒ $N_e = n_{\alpha} + n_{\beta}$
 - H₂O : $N_e = 10$ in a singlet state $\langle \hat{S}^2 \rangle = 0 \Rightarrow n_\alpha = n_\beta = 5$
 - $(H_2O)^+$: $N_e = 9$ in a doublet state $\langle \hat{S}^2 \rangle = 0.75 \Rightarrow n_\alpha = 5, n_\beta = 4$

- Number of particles: $[\hat{H}, \hat{N}] = 0$
 - $\Rightarrow N_e$ is constant
- Total spin S²: [Ĥ, Ŝ²] = 0
 ⇒ Work within a given eigenvalue of Ŝ²
- Spin projection on z: $[\hat{H}, \hat{S}_z] = 0$
 - ⇒ Defines $(n_{\alpha}, n_{\beta}) \Leftrightarrow (n_{\uparrow}, n_{\downarrow})$ compatible with the $\langle \hat{S}^2 \rangle$ value ⇒ $N_e = n_{\alpha} + n_{\beta}$
 - H₂O : $N_e = 10$ in a singlet state $\langle \hat{S}^2 \rangle = 0 \Rightarrow n_\alpha = n_\beta = 5$
 - $(H_2O)^+$: $N_e = 9$ in a doublet state $\langle \hat{S}^2 \rangle = 0.75 \Rightarrow n_\alpha = 5, n_\beta = 4$
- Spatial symmetries are special cases and not mandatory

- Number of particles: $[\hat{H}, \hat{N}] = 0$
 - $\Rightarrow N_e$ is constant
- Total spin S²: [Ĥ, Ŝ²] = 0
 ⇒ Work within a given eigenvalue of Ŝ²
- Spin projection on z: $[\hat{H}, \hat{S}_z] = 0$
 - ⇒ Defines $(n_{\alpha}, n_{\beta}) \Leftrightarrow (n_{\uparrow}, n_{\downarrow})$ compatible with the $\langle \hat{S}^2 \rangle$ value ⇒ $N_e = n_{\alpha} + n_{\beta}$
 - H₂O : $N_e = 10$ in a singlet state $\langle \hat{S}^2 \rangle = 0 \Rightarrow n_\alpha = n_\beta = 5$
 - $(H_2O)^+$: $N_e = 9$ in a doublet state $\langle \hat{S}^2 \rangle = 0.75 \Rightarrow n_\alpha = 5, n_\beta = 4$

• Spatial symmetries are special cases and not mandatory

• Atoms: spherical symmetry $[\hat{H}, \hat{L}^2] = 0$

- Number of particles: $[\hat{H}, \hat{N}] = 0$
 - $\Rightarrow N_e$ is constant
- Total spin S²: [Ĥ, Ŝ²] = 0
 ⇒ Work within a given eigenvalue of Ŝ²
- Spin projection on z: $[\hat{H}, \hat{S}_z] = 0$
 - ⇒ Defines $(n_{\alpha}, n_{\beta}) \Leftrightarrow (n_{\uparrow}, n_{\downarrow})$ compatible with the $\langle \hat{S}^2 \rangle$ value ⇒ $N_e = n_{\alpha} + n_{\beta}$
 - H₂O : N_e = 10 in a singlet state $\langle \hat{S}^2 \rangle$ = 0 \Rightarrow n_{α} = n_{β} = 5
 - $(H_2O)^+$: $N_e = 9$ in a doublet state $\langle \hat{S}^2 \rangle = 0.75 \Rightarrow n_\alpha = 5, n_\beta = 4$

• Spatial symmetries are special cases and not mandatory

- Atoms: spherical symmetry $[\hat{H}, \hat{L}^2] = 0$
- Linear molecule: rotational symmetry $[\hat{H}, \hat{L}_z] = 0$

- Number of particles: $[\hat{H}, \hat{N}] = 0$
 - $\Rightarrow N_e$ is constant
- Total spin S²: [Ĥ, Ŝ²] = 0
 ⇒ Work within a given eigenvalue of Ŝ²
- Spin projection on z: $[\hat{H}, \hat{S}_z] = 0$
 - ⇒ Defines $(n_{\alpha}, n_{\beta}) \Leftrightarrow (n_{\uparrow}, n_{\downarrow})$ compatible with the $\langle \hat{S}^2 \rangle$ value ⇒ $N_e = n_{\alpha} + n_{\beta}$
 - H₂O : N_e = 10 in a singlet state $\langle \hat{S}^2 \rangle$ = 0 \Rightarrow n_{lpha} = n_{eta} = 5
 - $(H_2O)^+$: $N_e = 9$ in a doublet state $\langle \hat{S}^2 \rangle = 0.75 \Rightarrow n_\alpha = 5, n_\beta = 4$

• Spatial symmetries are special cases and not mandatory

- Atoms: spherical symmetry $[\hat{H}, \hat{L}^2] = 0$
- Linear molecule: rotational symmetry $[\hat{H}, \hat{L}_z] = 0$
- Crystal: translational symmetry $[\hat{H}, \hat{T}_{\vec{a}}] = 0$

- Number of particles: $[\hat{H}, \hat{N}] = 0$
 - $\Rightarrow N_e$ is constant
- Total spin S²: [Ĥ, Ŝ²] = 0
 ⇒ Work within a given eigenvalue of Ŝ²
- Spin projection on z: $[\hat{H}, \hat{S}_z] = 0$
 - ⇒ Defines $(n_{\alpha}, n_{\beta}) \Leftrightarrow (n_{\uparrow}, n_{\downarrow})$ compatible with the $\langle \hat{S}^2 \rangle$ value ⇒ $N_e = n_{\alpha} + n_{\beta}$
 - H₂O : $N_e = 10$ in a singlet state $\langle \hat{S}^2 \rangle = 0 \Rightarrow n_\alpha = n_\beta = 5$
 - $(H_2O)^+$: $N_e = 9$ in a doublet state $\langle \hat{S}^2 \rangle = 0.75 \Rightarrow n_\alpha = 5, n_\beta = 4$

• Spatial symmetries are special cases and not mandatory

- Atoms: spherical symmetry $[\hat{H}, \hat{L}^2] = 0$
- Linear molecule: rotational symmetry $[\hat{H}, \hat{L}_z] = 0$
- Crystal: translational symmetry $[\hat{H}, \hat{T}_{\vec{a}}] = 0$
- A protein: nothing

• The wave function $|\Psi\rangle$ must be anti-symmetric

- The wave function $|\Psi
 angle$ must be anti-symmetric
- Slater determinants for α and β part is a good basis for $|\Psi\rangle$

$$|\Psi\rangle = \sum_{i_{\alpha},i_{\beta}} c_{i_{\alpha},i_{\beta}} |i_{\alpha}\rangle |i_{\beta}\rangle$$

$$\langle \mathbf{x}_{1}, \mathbf{x}_{2}, \cdots, \mathbf{x}_{n_{\omega}} | i_{\omega} \rangle = \frac{1}{\sqrt{n_{\omega}!}} \begin{vmatrix} \chi_{k_{1}}(\mathbf{x}_{1}) & \chi_{k_{2}}(\mathbf{x}_{1}) & \dots & \chi_{k_{n_{\omega}}}(\mathbf{x}_{1}) \\ \chi_{k_{1}}(\mathbf{x}_{2}) & \chi_{k_{2}}(\mathbf{x}_{2}) & \dots & \chi_{k_{n_{\omega}}}(\mathbf{x}_{2}) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_{k_{1}}(\mathbf{x}_{n_{\omega}}) & \chi_{k_{2}}(\mathbf{x}_{n_{\omega}}) & \dots & \chi_{k_{n_{\omega}}}(\mathbf{x}_{n_{\omega}}) \end{vmatrix}$$

 $\chi(\mathbf{x})$ are **spin-orbitals** $\mathbf{x}_i = (\omega, \mathbf{r}_i)$ collects spin $(\omega = \alpha, \beta)$ and space (\mathbf{r}_i) coordinate

- The wave function $|\Psi
 angle$ must be anti-symmetric
- Slater determinants for α and β part is a good basis for $|\Psi\rangle$

$$|\Psi\rangle = \sum_{i_{\alpha},i_{\beta}} c_{i_{\alpha},i_{\beta}} |i_{\alpha}\rangle |i_{\beta}\rangle$$

$$\langle \mathbf{x}_{1}, \mathbf{x}_{2}, \cdots, \mathbf{x}_{n_{\omega}} | i_{\omega} \rangle = \frac{1}{\sqrt{n_{\omega}!}} \begin{vmatrix} \chi_{k_{1}}(\mathbf{x}_{1}) & \chi_{k_{2}}(\mathbf{x}_{1}) & \dots & \chi_{k_{n_{\omega}}}(\mathbf{x}_{1}) \\ \chi_{k_{1}}(\mathbf{x}_{2}) & \chi_{k_{2}}(\mathbf{x}_{2}) & \dots & \chi_{k_{n_{\omega}}}(\mathbf{x}_{2}) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_{k_{1}}(\mathbf{x}_{n_{\omega}}) & \chi_{k_{2}}(\mathbf{x}_{n_{\omega}}) & \dots & \chi_{k_{n_{\omega}}}(\mathbf{x}_{n_{\omega}}) \end{vmatrix}$$

 $\chi(\mathbf{x})$ are spin-orbitals $\mathbf{x}_i = (\omega, \mathbf{r}_i)$ collects spin $(\omega = \alpha, \beta)$ and space (\mathbf{r}_i) coordinate • In practice $\chi(\mathbf{x}) = \psi(\mathbf{r})|\omega\rangle$ with $\langle \omega'|\omega\rangle = \delta_{\omega,\omega'}$

$$\underbrace{\psi_i(\mathbf{r})}_{\text{MOs}} = \sum_m C_{\mu i} \underbrace{\phi_\mu(\mathbf{r})}_{\text{AOs}}, \quad \langle \psi_j | \psi_i \rangle = \delta_{ij} \Rightarrow \text{ MO basis}$$

- The wave function $|\Psi
 angle$ must be anti-symmetric
- Slater determinants for α and β part is a good basis for $|\Psi\rangle$

$$|\Psi\rangle = \sum_{i_{\alpha},i_{\beta}} c_{i_{\alpha},i_{\beta}} |i_{\alpha}\rangle |i_{\beta}\rangle$$

$$\langle \mathbf{x}_1, \mathbf{x}_2, \cdots, \mathbf{x}_{n_\omega} | i_\omega \rangle = \frac{1}{\sqrt{n_\omega!}} \begin{vmatrix} \chi_{k_1}(\mathbf{x}_1) & \chi_{k_2}(\mathbf{x}_1) & \cdots & \chi_{k_{n_\omega}}(\mathbf{x}_1) \\ \chi_{k_1}(\mathbf{x}_2) & \chi_{k_2}(\mathbf{x}_2) & \cdots & \chi_{k_{n_\omega}}(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_{k_1}(\mathbf{x}_{n_\omega}) & \chi_{k_2}(\mathbf{x}_{n_\omega}) & \cdots & \chi_{k_{n_\omega}}(\mathbf{x}_{n_\omega}) \end{vmatrix}$$

 $\chi(\mathbf{x})$ are spin-orbitals $\mathbf{x}_i = (\omega, \mathbf{r}_i)$ collects spin $(\omega = \alpha, \beta)$ and space (\mathbf{r}_i) coordinate • In practice $\chi(\mathbf{x}) = \psi(\mathbf{r})|\omega\rangle$ with $\langle \omega'|\omega\rangle = \delta_{\omega,\omega'}$

$$\underbrace{\psi_i(\mathbf{r})}_{\text{MOs}} = \sum_m C_{\mu i} \underbrace{\phi_\mu(\mathbf{r})}_{\text{AOs}}, \quad \langle \psi_j | \psi_i \rangle = \delta_{ij} \Rightarrow \text{ MO basis}$$

• Need for a AO basis set $\mathcal{B} = \{\phi_{\mu}(\mathbf{r}), \mu = 1, N_{\mathcal{B}}\}$

Second quantized operators and basis set

- Assume $\mathcal{B} = \{\chi_k(\mathbf{x}), k = 1, N_{\mathcal{B}}\}$ with $\langle \chi_j | \chi_i \rangle = \delta_{ij}$ is known
- Work in the Fock space $[a_i^{\dagger}, a_j]_+ = \delta_{ij}$

$$H = \sum_{i,j} a_i^{\dagger} a_j \left(t_{ij} + v_{ij} \right) + \frac{1}{2} \sum_{ijkl} a_k^{\dagger} a_l^{\dagger} a_j a_i V_{ij}^{kl}$$

- The integrals one needs to evaluate are then
 - The one body integrals

$$t_{ij} = \int d\mathbf{r} \psi_i(\mathbf{r}) \left(-\frac{1}{2} \Delta \right) \psi_j(\mathbf{r})$$
$$v_{ij} = -\sum_{\kappa} \int d\mathbf{r} \psi_i(\mathbf{r}) \frac{Z_{\kappa}}{|\mathbf{r} - \mathbf{R}_{\kappa}|} \psi_j(\mathbf{r})$$

The two-body integrals

$$V_{ij}^{kl} = \int \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2 \psi_i(\mathbf{r}_1) \psi_j(\mathbf{r}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi_k(\mathbf{r}_1) \psi_l(\mathbf{r}_2)$$

What will guide us to design the basis set ?

• Physical motivations

- Shell model in chemistry: each atoms has "its own orbitals"
 ⇒ Atom-centered basis set
- What do we know about coulomb systems ?
 ⇒ some properties of exact solutions
- We need a basis for both the occupied and virtual orbitals
 ⇒ corresponds to "HF" and correlated wave functions
- Practical constraints
 - **A LOT** of V_{ii}^{kl} to compute $\propto (N_{\mathcal{B}})^4$
 - V_{ii}^{kl} is an integral in \mathbb{R}^6
 - Numerical integration is not feasible
 - Need analytical formula for V_{ij}^{kl}

The basis set exchange website

sis Set Exchange (BSE × +	ł									
→ C' û	🗊 🔒 https://www.bas	sissetexchange.org								
t visited 😻 Getting Starte	.d									
Rasis Set	Fychange	Download GitHub	Feedback	About F	- Heln - Rea	uest a Rasi	s set			
	Exchange									
All roles	- All									
		_	Total found	d: 327 basis	s sets					
2ZaPa-NR										
2ZaPa-NR-CV			Н							
3-21G										
3ZaPa-NR				Be						
3ZaPa-NR-CV			Na	Mg						
4ZaPa-NR				28	21	22	23	24	25	
4ZaPa-NR-CV			К	Ca	Sc	Ti	v	Cr	Mn	Fe
5-21G			37 Rh	31 Sr	31 V	7.	n Nh	Ma	Te	р.
5ZaPa-NR			100	54		72		74	22	
5ZaPa-NR-CV			Cs	Ba		Hf	Та	w	Re	0
6-21G			87	55		104	165	105	147	
6-31++G			Fr	Ra		Rf	Db	Sg	Bh	H
6-31++G*									-	
6-31++G**						La	Ce	Pr	Nd	Pn
6-31+G							**	91	**	
6-31+G*						Ac	Th	Pa	U	N
6-31+G**										
6-311++G										
6-311++G(2d,2p)										
6-311++G(307,3pd)										
6-311++6*										
0-311++6**										
6.21146										

We have a looooot of basis sets

🔀 Basis S	et Exchange (BSE ×	+										
$\overleftarrow{\left(\leftrightarrow \right) }$	ଟ ଜ 	The https://www.basissetexchange.org										
☆ Most \	/isited 🟮 Getting Starl	ted										
26	Basis Set	Exchange	Download GitHub	Feedback	About H	elp - Req	uest a Basi	s set				
	All roles	- All	•	Total found	: 327 basis	sets						
	2ZaPa-NR		- N-		_	_	,					
	2ZaPa-NR-CV			н								
	3-21G			1								
	3ZaPa-NR			L	Be							
	3ZaPa-NR-CV			Na	Mg							
	4ZaPa-NR				20	21	22	23	24	25	26	
	4ZaPa-NR-CV			К	Ca	Sc	Ti	v	Cr	Mn	Fe	
	5-21G			37 DL	31 6-	31 V	7.	41 NL	a Ma	о Т-		
	5ZaPa-NR			KD "	31						Ru	
	5ZaPa-NR-CV			Cs	Ba		Hf	Та	w	Re	Os	
	6-21G			87	85		104	105	106	107	105	
	6-31++G			Fr	Ra		Rf	Db	Sg	Bh	Hs	
	6-31++G*											
	6-31++G**						La	Ce	Pr	Nd	Pm	
	6-31+G							**		92	*1	
	6-31+G*						Ac	Th	Pa	U	Np	
	6-31+G**											
	6-311++G											
	6-311++G(2d,2p)											
	6-311++G(3df,3pd)											
	6-311++G*											
	6-311++G**											
	6 211+0											

We have a looooot of basis sets

sis Set Exchange (BSE ×	+									
→ C' 俞	⑦ ▲ https://www.	basissetexchange.org								
		jj								
ost Visited 😻 Getting S	tarted	▲ https://www.basissetexchange.org Xchange Download Gittyte Feedback ▲ All Total found: 327 basis sets H Ba Na K Ca Sc Ti V Cr Ma Fe								
PRocie Se	t Exchange		Fredhards.	Ab						
			reedback	About n	elp · Req	Jest a Basi	s set			
All roles	- All									
		-	Total found	327 basis	sets					
2ZaPa-NR					_					
2ZaPa-NR-CV			н							
3-21G										
3ZaPa-NR				DV						
3ZaPa-NR-CV			Na	Mg		_				
4ZaPa-NR				20	21	22	23	24	25	26
4ZaPa-NR-CV			К	Ca	Sc	Ti	v	Cr	Mn	Fe
5-21G			37	м	31			a 14	- 0 T	
5ZaPa-NR			RD	Sr	Y	Zr	ND	MO	IC	Ru
5ZaPa-NR-CV			Cs "	Ba		Hf	Ta	W	Re	Os
6-21G			87	85	i	104	105	106	107	105
6-31++G			Fr	Ra		Rf	Db	Sg	Bh	Hs
6-31++G*										
6-31++G**						1.4	· · · ·	Pr	Nd	Pm
6-31+G							93		92	83
6-31+G*						Ac	Th	Pa	U	Np
6-31+G**										
6-311++G										
6-311++G(2d,2p)										
6-311++G(3df,3pd)										
6-311++G*										
6-311++G**										
6 21110										

Two questions we will try to answer

- Why are there so many basis sets ?
- What are the typical differences between these basis sets ?
- How are they built ?

Physical motivations

What do we know about exact solutions of Coulomb systems ?

• The density decays as $e^{-\alpha |\mathbf{r}|}$ (with $\alpha = 2\sqrt{2I_0}$, $I_0 = IP$)

Physical motivations

What do we know about exact solutions of Coulomb systems ?

- The density decays as $e^{-\alpha |\mathbf{r}|}$ (with $\alpha = 2\sqrt{2I_0}$, $I_0 = IP$)
- **2** The shape of the exact wave function near a nucleus $\{\mathbf{R}_k, Z_k\}$

$$\Psi(\mathbf{r}) = \Psi(\mathbf{R}_k) \left(1 - Z_k |\mathbf{r} - \mathbf{R}_k| + \cdots\right)$$

 \Rightarrow This is the so-called **electron-nuclear cusp**

Physical motivations

What do we know about exact solutions of Coulomb systems ?

- The density decays as $e^{-\alpha |\mathbf{r}|}$ (with $\alpha = 2\sqrt{2I_0}$, $I_0 = IP$)
- **2** The shape of the exact wave function near a nucleus $\{\mathbf{R}_k, Z_k\}$

$$\Psi(\mathbf{r}) = \Psi(\mathbf{R}_k) \left(1 - Z_k |\mathbf{r} - \mathbf{R}_k| + \cdots\right)$$

 \Rightarrow This is the so-called **electron-nuclear cusp**

O Hydrogen-like eigenfunctions behave as $e^{-Z_k r} = 1 - Z_k r + \cdots$

$$\left(-\frac{1}{2}\Delta - \frac{Z_k}{r}\right)\phi_{nlm}(\mathbf{r}) = E\phi_{nlm}(\mathbf{r})$$

$$\phi_{nlm}(\mathbf{r}) = L_n^l(r) Y_l^m(\theta_k, \phi_k) e^{-\mathbf{Z}_k r}$$

 $L_n^l(r)$ a Laguerre polynom $Y_l^m(\theta, \phi)$ a spherical harmonic

Example for the hydrogen atom $(Z_k = 1)$

$$\phi_{1s}(r) = \frac{1}{\sqrt{\pi}} e^{-r}$$

$$\phi_{2s}(r) = \frac{1}{8\sqrt{\pi}} (1 - 2r) e^{-r/2}$$

$$\phi_{2p_0}(r) = \frac{1}{4\sqrt{2\pi}} r \cos(\theta) e^{-r/2}$$



Atom centered basis set for molecule

- Hydrogenoid function (or Slater orbitals) have nice properties
 - $\propto e^{-\alpha |\mathbf{r}|}$
 - $\{\phi_{nlm}(\mathbf{r})\}$ form a complete basis: "just need to increase n"
 - easy to impose the electron-nuclear cusp
- Natural idea for a molecule: atom centered basis set

• you "attach" to each atom $\{\mathbf{R}_k, Z_k\}$ a set of functions



$$\mathbf{r} \rightarrow \mathbf{r} - \mathbf{R}_k$$

 $\phi_{1s}^k(\mathbf{r}) = \frac{Z_k^{3/2}}{\sqrt{\pi}} e^{-Z_k |\mathbf{r} - \mathbf{R}_k}$

Intuitive idea

- Hydrogenoid function (or Slater orbitals) have nice properties
 - $\propto e^{-\alpha |\mathbf{r}|}$
 - $\{\phi_{nlm}(\mathbf{r})\}$ form a complete basis: "just need to increase n"
 - easy to impose the electron-nuclear cusp
- Natural idea for a molecule: atom centered basis set

• you "attach" to each atom $\{\mathbf{R}_k, Z_k\}$ a set of functions



Intuitive idea

- Hydrogenoid function (or Slater orbitals) have nice properties
 - $\propto e^{-\alpha |\mathbf{r}|}$
 - $\{\phi_{nlm}(\mathbf{r})\}$ form a complete basis: "just need to increase n"
 - easy to impose the electron-nuclear cusp
- Natural idea for a molecule: atom centered basis set

• you "attach" to each atom $\{\mathbf{R}_k, \mathbf{Z}_k\}$ a set of functions



$$\mathbf{r} \rightarrow \mathbf{r} - \mathbf{R}_{k}$$

$$\phi_{1s}^{k}(\mathbf{r}) = \frac{Z_{k}^{3/2}}{\sqrt{\pi}} e^{-Z_{k}|\mathbf{r} - \mathbf{R}_{k}|}$$

• Problem: V_{ii}^{kl} are not analytical with Slater orbitals $(e^{-\alpha |\mathbf{r}|})$

- Problem: V_{ij}^{kl} are not analytical with Slater orbitals $(e^{-\alpha |\mathbf{r}|})$
- With Gaussian functions all integrals are analytical

$$\begin{split} \phi(\mathbf{r}) &= (x - R_x)^{a_x} (y - R_y)^{a_y} (z - R_z)^{a_z} e^{-\alpha (\mathbf{r} - \mathbf{R}_k)^2} \\ \frac{1}{r_{12}} &= \frac{2}{\sqrt{\pi}} \int du \ e^{-u^2 (r_{12})^2} \quad \text{replace the annoying } 1/r_{12} \text{ by Gaussian} \\ \int d\mathbf{r}_1 d\mathbf{r}_2 \rightarrow \left(\int dx_1 \int dx_2 \right) \times \left(\int dy_1 \int dy_2 \right) \times \left(\int dz_1 \int dz_2 \right) \\ \int du \rightarrow \text{ numerical using orthonormal polynoms (Ex: Rys)} \end{split}$$

۲

Why we don't do exactly that

- Problem: V_{ij}^{kl} are not analytical with Slater orbitals $(e^{-\alpha |\mathbf{r}|})$
- With Gaussian functions all integrals are analytical

$$\phi(\mathbf{r}) = (x - R_x)^{a_x} (y - R_y)^{a_y} (z - R_z)^{a_z} e^{-\alpha (\mathbf{r} - \mathbf{R}_k)^2}$$

$$\frac{1}{r_{12}} = \frac{2}{\sqrt{\pi}} \int du \ e^{-u^2 (r_{12})^2} \quad \text{replace the annoying } 1/r_{12} \text{ by Gaussian}$$

$$\int d\mathbf{r}_1 d\mathbf{r}_2 \rightarrow \left(\int dx_1 \int dx_2\right) \times \left(\int dy_1 \int dy_2\right) \times \left(\int dz_1 \int dz_2\right)$$

$$\int du \rightarrow \text{ numerical using orthonormal polynoms (Ex: Rys)}$$
We fit Slater-type orbitals with Gaussians

$$e^{-\alpha|\mathbf{r}|} \approx \sum_{m} c_{m} e^{-\alpha_{m}\mathbf{r}^{2}}$$

- Problem: V_{ij}^{kl} are not analytical with Slater orbitals $(e^{-\alpha |\mathbf{r}|})$
- With Gaussian functions all integrals are analytical

$$\phi(\mathbf{r}) = (x - R_x)^{a_x} (y - R_y)^{a_y} (z - R_z)^{a_z} e^{-\alpha (\mathbf{r} - \mathbf{R}_k)^2}$$

$$\frac{1}{r_{12}} = \frac{2}{\sqrt{\pi}} \int du \ e^{-u^2 (r_{12})^2} \quad \text{replace the annoying } 1/r_{12} \text{ by Gaussian}$$

$$\int d\mathbf{r}_1 d\mathbf{r}_2 \rightarrow \left(\int dx_1 \int dx_2\right) \times \left(\int dy_1 \int dy_2\right) \times \left(\int dz_1 \int dz_2\right)$$

$$\int du \rightarrow \text{ numerical using orthonormal polynoms (Ex: Rys)}$$

• We fit Slater-type orbitals with Gaussians

$$e^{-\alpha|\mathbf{r}|} \approx \sum_{m} c_{m} e^{-\alpha_{m}\mathbf{r}^{2}}$$

• Use a set of $\{c_m, \alpha_m\}$ to reproduce $e^{-\alpha |\mathbf{r}|}$

- Problem: V_{ij}^{kl} are not analytical with Slater orbitals $(e^{-\alpha |\mathbf{r}|})$
- With Gaussian functions all integrals are analytical

$$\begin{split} \phi(\mathbf{r}) &= (x - R_x)^{a_x} (y - R_y)^{a_y} (z - R_z)^{a_z} e^{-\alpha (\mathbf{r} - \mathbf{R}_k)^2} \\ \frac{1}{r_{12}} &= \frac{2}{\sqrt{\pi}} \int du \ e^{-u^2 (r_{12})^2} \quad \text{replace the annoying } 1/r_{12} \text{ by Gaussian} \\ \int d\mathbf{r}_1 d\mathbf{r}_2 \rightarrow \left(\int dx_1 \int dx_2 \right) \times \left(\int dy_1 \int dy_2 \right) \times \left(\int dz_1 \int dz_2 \right) \\ \int du \rightarrow \text{ numerical using orthonormal polynoms (Ex: Rys)} \end{split}$$

• We fit Slater-type orbitals with Gaussians

$$e^{-\alpha|\mathbf{r}|} \approx \sum_{m} c_{m} e^{-\alpha_{m}\mathbf{r}^{2}}$$

- Use a set of $\{c_m, \alpha_m\}$ to reproduce $e^{-\alpha |\mathbf{r}|}$
- A basis set \mathcal{B} for an atom Z_k : could be **2** parameters

- Problem: V_{ij}^{kl} are not analytical with Slater orbitals $(e^{-\alpha |\mathbf{r}|})$
- With Gaussian functions all integrals are analytical

$$\begin{split} \phi(\mathbf{r}) &= (x - R_x)^{a_x} (y - R_y)^{a_y} (z - R_z)^{a_z} e^{-\alpha (\mathbf{r} - \mathbf{R}_k)^2} \\ \frac{1}{r_{12}} &= \frac{2}{\sqrt{\pi}} \int du \ e^{-u^2 (r_{12})^2} \quad \text{replace the annoying } 1/r_{12} \text{ by Gaussian} \\ \int d\mathbf{r}_1 d\mathbf{r}_2 \rightarrow \left(\int dx_1 \int dx_2 \right) \times \left(\int dy_1 \int dy_2 \right) \times \left(\int dz_1 \int dz_2 \right) \\ \int du \rightarrow \text{ numerical using orthonormal polynoms (Ex: Rys)} \end{split}$$

• We fit Slater-type orbitals with Gaussians

$$e^{-\alpha|\mathbf{r}|} \approx \sum_{m} c_{m} e^{-\alpha_{m}\mathbf{r}^{2}}$$

- Use a set of $\{c_m, \alpha_m\}$ to reproduce $e^{-\alpha |\mathbf{r}|}$
- A basis set \mathcal{B} for an atom Z_k : could be 2 parameters
 - The maximum principal quantum number n_{max} for $\phi_{nlm}(\mathbf{r})$

- Problem: V_{ij}^{kl} are not analytical with Slater orbitals $(e^{-\alpha |\mathbf{r}|})$
- With Gaussian functions all integrals are analytical

$$\begin{split} \phi(\mathbf{r}) &= (x - R_x)^{a_x} (y - R_y)^{a_y} (z - R_z)^{a_z} e^{-\alpha (\mathbf{r} - \mathbf{R}_k)^2} \\ \frac{1}{r_{12}} &= \frac{2}{\sqrt{\pi}} \int du \ e^{-u^2 (r_{12})^2} \quad \text{replace the annoying } 1/r_{12} \text{ by Gaussian} \\ \int d\mathbf{r}_1 d\mathbf{r}_2 \rightarrow \left(\int dx_1 \int dx_2 \right) \times \left(\int dy_1 \int dy_2 \right) \times \left(\int dz_1 \int dz_2 \right) \\ \int du \rightarrow \text{ numerical using orthonormal polynoms (Ex: Rys)} \end{split}$$

• We fit Slater-type orbitals with Gaussians

$$e^{-\alpha|\mathbf{r}|} \approx \sum_{m} c_{m} e^{-\alpha_{m}\mathbf{r}^{2}}$$

- Use a set of $\{c_m, \alpha_m\}$ to reproduce $e^{-\alpha |\mathbf{r}|}$
- A basis set \mathcal{B} for an atom Z_k : could be 2 parameters
 - The maximum principal quantum number n_{max} for $\phi_{nlm}(\mathbf{r})$
 - The maximum number of Gaussians to represent $e^{-\alpha |\mathbf{r}|}$

Why we don't do that neither ?

• For an atom of charge Z_k , $e^{-Z_k r}$ are **too tight**

$$H(Z_k, N_e) = \sum_{i=1}^{N_e} \underbrace{\left(-\frac{1}{2}\Delta_i - \frac{Z_k}{|\mathbf{r}_i|}\right)}_{h(\mathbf{r}_i, Z_k) \text{ purely attractive}} + \underbrace{\sum_{i=1}^{N_e} \sum_{j>i}^{N_e} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}}_{\text{purely repulsive}}$$

- $e^{-Z_k r}$ types are eigenfunctions of $h(\mathbf{r}, Z_k)$
- The repulsion between electrons makes the density expand
- We need to take into account in average $\frac{1}{|\mathbf{r}_i \mathbf{r}_i|}$
- Mean-field procedure: Hartree Fock
- Idea: use the "Hartree-Fock" eigenfunctions as a basis

The HF equations i a nutshell

• The HF wave function is a single Slater determinant

$$|\Phi\rangle = a^{\dagger}_{\chi_1} \cdots a^{\dagger}_{\chi_{N_e}} |0\rangle$$

• Minimize the variational energy with respect to $\{\chi_i\}$

$$E_{\mathsf{HF}} = \min_{\{\chi\}} \frac{\langle \Phi | H | \Phi \rangle}{\langle \Phi | \Phi \rangle}$$

• Leads to a self-consistent one-body eigenvalue equation

$$\frac{\partial E_{\mathsf{HF}}}{\partial \chi_i} = 0 \Leftrightarrow F |\chi_i\rangle = \epsilon_i |\chi_i\rangle$$

$$F = \underbrace{-\frac{1}{2}\Delta + v_{ne}(\mathbf{r}, \{Z_k, \mathbf{R}_k\})}_{h(\mathbf{r}, \{Z_k, \mathbf{R}_k\})} + \underbrace{J[\{\chi\}] - K[\{\chi\}]}_{\text{Coulomb and Exchange: repulsion}}$$

Example of solutions: the Li atom $(Z_k = 3)$



Example of solutions: the Li atom $(Z_k = 3)$



Few example or the core/valence splitting at HF level

Remember: IP of hydrogen is 0.5 a.u.


Optimizing the basis sets at HF level

- We optimize the basis set for the HF energy !
- Expand the MOs on AOs (⇔ Gaussians × polynom)

$$\psi_i(\mathbf{x}) = \sum_{\mu=1}^{N_B} C_{i\mu} \phi_{\mu}(\mathbf{r})$$

$$\phi_{\mu}(\mathbf{r}) = x^{a_x} y^{a_y} z^{a_z} \sum_{m}^{m_{max}} c_m e^{-\alpha_m(\mathbf{r})^2}$$

• An AO basis set is then defined by

• a maximum "angular momentum" I_{max} for $a_x + a_y + a_z$ Ex: "s" $\Leftrightarrow I_{max} = 0$ $\phi_{\mu}(\mathbf{r}) = \sum_{m}^{m_{max}} c_m e^{-\alpha_m(\mathbf{r})^2}$ Ex: "p" $\Leftrightarrow I_{max} = 1$ $\phi_{\mu}(\mathbf{r}) = z \sum_{m}^{m_{max}} c_m e^{-\alpha_m(\mathbf{r})^2}$ • the number m_{max} of "Primitive" Gaussians for each $\phi_{\mu}(\mathbf{r})$ • For a given set of m_{max} and I_{max} $\{c_m, \alpha_m\} = \operatorname*{argmin}_{\{c,\alpha\}} \frac{\langle \mathrm{HF}|\mathrm{H}|\mathrm{HF}\rangle}{\langle \mathrm{HF}|\mathrm{HF}\rangle}$

Why are there sooooo many basis sets

Optimizing for **HF is not enough**: only the occupied are good Optimize the energy of **correlated** wave functions (Ex: CISD)

$$\min_{\{c_m,\alpha_m\}} \frac{\langle \text{CISD} | H | \text{CISD} \rangle}{\langle \text{CISD} | \text{CISD} \rangle}$$

Why are there sooooo many basis sets

Optimizing for **HF is not enough**: only the occupied are good Optimize the energy of **correlated** wave functions (Ex: CISD)

$$\min_{\{c_m,\alpha_m\}} \frac{\langle \text{CISD} | \mathcal{H} | \text{CISD} \rangle}{\langle \text{CISD} | \text{CISD} \rangle}$$

There are **many ways** of doing that:

- Addition of higher angular momentum (ex: "p" for H)
 - Allows "polarization" of the density
 - Allows for "angular" correlation effects
- More diffuse functions
 - Describe orbital relaxation for charged states
 - Mandatory to describe diffuse excited states
- More tight functions
 - Core-valence and core-core correlation
 - Mandatory for core properties (density at the nucleus)
- Do you consider also cations and anions of the atom ?
- Do you want valence excited states ?

A very used family of basis sets: the cc-pVXZ

Dunning et. al. introduced the Correlation Consistent basis:

the cc-pVXZ family of basis sets

- cc : Correlation Consistent
- **p** : polarization *i.e.* higher angular momentum than valence
- V : valence
- XZ : number of functions per valence shell
- Quality: cc-pVDZ < cc-pVTZ < cc-pVQZ etc ...
- Other variants
 - the aug-cc-pVXZ for diffuse functions
 - the cc-pCVXZ for core (*i.e.* tight) functions

Ex: **He atom**, valence: $1s^2$ in the **cc-pVDZ** (5 AOs)

- DZ : 2 orbitals for each valence shell → 2 "S" functions
 - 1 valence $\phi_{1s}(\mathbf{r})$ made of 4 Gaussians

$$\phi_{1s}(\mathbf{r}) = 0.024e^{-38.36r^2} + 0.155e^{-5.77r^2} + 0.47e^{-1.24r^2} + 0.51e^{-0.29r^2}$$

• 1 extra "S" function made of 1 Gaussian for correlation

$$\phi_{\mathcal{S}}(\mathbf{r}) = e^{-0.029\mathbf{r}^2}$$

1 "polarization" function *i.e.* of higher angular momentum
 1 "P" function for correlation and polarization

$$\phi_{p_x}(\mathbf{r}) = x \ e^{-1.275\mathbf{r}^2}, \quad \phi_{p_y}(\mathbf{r}) = y \ e^{-1.275\mathbf{r}^2}, \quad \phi_{p_z}(\mathbf{r}) = z \ e^{-1.275\mathbf{r}^2}$$

- Coefficients/exponents have been optimized at correlated level
- cc-pVTZ: 15 AOs
 - 3 S functions
 - 2 P functions
 - 1 D function

cc-pVQZ: 35 AOs

- 4 S functions
- 3 P functions
- 2 D function
- 1 F function

A typical correlated calculation

FCI total energy of the He atom with the cc-pVXZ (X=D,T,Q,5)



The slow convergence of correlation effects: the e - e cusp

Why correlation energy converges so slow ?

- Coulomb **divergence** when $r_{12} \rightarrow 0$
- The exact wave function behaves as

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi(\mathbf{r}_1, r_{12} = 0) \left(1 + \frac{1}{2}|\mathbf{r}_1 - \mathbf{r}_2| + \cdots\right)$$

- Universal behaviour at $r_{12} \approx 0$: e e cusp
- Problem: $f(\mathbf{r}_1, \mathbf{r}_2) = |\mathbf{r}_1 \mathbf{r}_2|$ converges poorly in a basis set
- The correlation energy converges poorly as $\left(\frac{1}{l_{max}}\right)^3$
- In a finite basis set, the wave functions have no cusp











Correlation effects in a finite basis set \mathcal{B}

- Within \mathcal{B} : correlation (Ex: FCI) digs the "Coulomb hole"
 - HF is a mean field model: independent particle model

$$\mathbf{n}_{\mathsf{HF}}^{(2)}(\mathbf{r}_1,\mathbf{r}_2) \propto \mathbf{n}_{\mathsf{HF}}^{(1)}(\mathbf{r}_1) \times \mathbf{n}_{\mathsf{HF}}^{(1)}(\mathbf{r}_2)$$

- $n_{\text{HF}}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ too large at small r_{12}
- Correlation lowers $n^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ at $r_{12} \approx 0$
- BUT: Finite basis set \rightarrow no e e cusp even at FCI
- Improving the basis set \rightarrow dig deeper the Coulomb hole
- Slow convergence of the $n^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ at $r_{12} \approx 0$ with \mathcal{B}
- Overestimate the Coulomb repulsion between e

What about energy differences ?

Atomic Ionization Potential for Z = 5,10 at FCI with cc-pVXZ

$$IP = E(N_e, Z) - E(N_e - 1, Z), \text{ with } N_e = Z$$

Atomic lonization Potential for Z = 5,10 at FCI with cc-pVXZ

$$IP = E(N_e, Z) - E(N_e - 1, Z), \text{ with } N_e = Z$$



Atomic Ionization Potential for Z = 5,10 at FCI with cc-pVXZ

$$IP = E(N_e, Z) - E(N_e - 1, Z), \text{ with } N_e = Z$$



Atomic lonization Potential for Z = 5,10 at FCI with cc-pVXZ

$$IP = E(N_e, Z) - E(N_e - 1, Z), \text{ with } N_e = Z$$



Atomic lonization Potential for Z = 5,10 at FCI with cc-pVXZ

$$IP = E(N_e, Z) - E(N_e - 1, Z), \text{ with } N_e = Z$$



Correlation effects for energy differences

- Slow convergence of the IP with the basis set
- cc-pV5Z quality is needed to reach 1 kcal/mol for Z > 7
- Error at FCI has always the same sign
- The cation is always favoured in a given basis set
 - one electron less
 - less electrons pairs
 - less correlation effects
- What about energy differences in molecules ?

 $\mathsf{AE}(AB) = \mathsf{E}(AB) - (\mathsf{E}(A) + \mathsf{E}(B))$

Deviation with respect to the Complete Basis Set (CBS) AE For these systems $CCSD(T) \approx FCI \rightarrow only$ basis set error "Small" systems: < 10 atoms, < 30 correlated *e* (frozen core)

 $\mathsf{AE}(AB) = \mathsf{E}(AB) - (\mathsf{E}(A) + \mathsf{E}(B))$

Deviation with respect to the Complete Basis Set (CBS) AE For these systems $CCSD(T) \approx FCI \rightarrow$ only basis set error "Small" systems: < 10 atoms, < 30 correlated *e* (frozen core) cc-pVTZ \approx 100 MOs, cc-pVQZ \approx 200 MOs, cc-pV5Z \approx 300 MOs

 $\mathsf{AE}(AB) = \mathsf{E}(AB) - (\mathsf{E}(A) + \mathsf{E}(B))$

Deviation with respect to the Complete Basis Set (CBS) AE For these systems $CCSD(T) \approx FCI \rightarrow$ only basis set error "Small" systems: < 10 atoms, < 30 correlated *e* (frozen core) cc-pVTZ \approx 100 MOs, cc-pVQZ \approx 200 MOs, cc-pV5Z \approx 300 MOs



 $\mathsf{AE}(AB) = \mathsf{E}(AB) - (\mathsf{E}(A) + \mathsf{E}(B))$

Deviation with respect to the Complete Basis Set (CBS) AE For these systems $CCSD(T) \approx FCI \rightarrow$ only basis set error "Small" systems: < 10 atoms, < 30 correlated *e* (frozen core) cc-pVTZ \approx 100 MOs, cc-pVQZ \approx 200 MOs, cc-pV5Z \approx 300 MOs



→ CCSD(T)/cc-pVDZ: MAD = 14.29 kcal.mol⁻¹ → CCSD(T)/cc-pVTZ: MAD = 6.06 kcal.mol⁻¹ → CCSD(T)/cc-pVQZ: MAD = 2.50 kcal.mol⁻¹

Method	Mean Abs. Dev.	Chemically Accurate
CCSD(T)/cc-pVDZ	14.29	2
CCSD(T)/cc-pVTZ	6.06	2
CCSD(T)/cc-pVQZ	2.50	9
CCSD(T)/cc-pV5Z	1.28	21

A few remarks on basis set convergence

- For these systems CCSD(T) ≈ FCI
- "Only" error is the basis set B
- Error with respect to CBS have always the same sign
- Atomic basis sets:
 - atoms better described than molecules
 - more correlation in molecules than atoms
 - the AE are always underestimated

Conclusion on basis sets

- Try to fit "Correlated-like" orbitals
- \bullet We use polynoms \times Gaussian functions
- Integrals are analytical
- Many basis sets have been designed according
 - the property one is targetting (valence, core etc ...)
 - the type of atoms (light or heavy atom ?)
 - type of Hamiltonian used (WFT, DFT, relativity etc ...)
 - what level of calculation is used (max angular momentum)
- The correlation consistent basis sets (cc-pVXZ)
 - designed for correlated calculations
 - allows for a quite systematic convergence
- Correlation effects converge slowly with X
 - short-range correlation effects (*e e* cusp)
 - atom-centered basis set bad for molecules
 - Explicitely correlated methods (F12) help in fixing the problem

The notion of computational scaling

The methods can be characterized by their computational scaling: One looks at typical bottlenecks in the algorithm **CPU time** bottlenecks

- Diagonalization of an $N \times N$ matrix ($\propto N^3$)
- Handling of two-electron integrals V_{ij}^{kl} ($\propto N_B^4$)
- Comparison between determinants etc ...

Memory type bottleneck

- Storing a $N \times N$ matrix ($\propto N^2$)
- Storing the V_{ij}^{kl} ($\propto N_B^4$)
- Accessing randomly to the RAM (wait for data to come)
- Disk access

Formal scalings

The "formal" scaling of the methods are

- Hartree Fock: $(N_{\mathcal{B}})^4$ (due to the V_{ij}^{kl})
- MP2: $(N_{\mathcal{B}})^5$ (due to the AO \rightarrow MO V_{ij}^{kl} transformation)
- **CCSD**: $(N_{\mathcal{B}})^6$ (due the contraction of V_{ij}^{kl} with T_{ij}^{ab})
- **CCSD(T)**: $(N_{\mathcal{B}})^7$ (due to the contribution of the triples)
- **CAS**: e^{N_B} (due to the complete active space)
- selected CI: αe^{N_B} with $\alpha \ll 1$ (due to the selection)

Nevertheless, calculations with a hundred of atoms are feasible within $\mathsf{CCSD}(\mathsf{T})$...

 \Rightarrow we exploit the locality of Gaussians and correlation

The two-electron integrals for a large system

• Key quantity are the $V^{
u\sigma}_{\mu\lambda}$ in the AO basis

$$V_{\mu\lambda}^{\nu\sigma} = (\mu\nu|\lambda\sigma) = \int d\mathbf{r}_1 d\mathbf{r}_2 \phi_\mu(\mathbf{r}_1) \phi_\nu(\mathbf{r}_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_\lambda(\mathbf{r}_2) \phi_\sigma(\mathbf{r}_2)$$

- AO are attached to a nucleus: $\phi_{\mu}({f r}) \propto e^{-lpha ({f r}-{f R}_k)^2}$
- Therefore for a couple μ, ν

$$\phi_{\mu}(\mathbf{r})\phi_{\nu}(\mathbf{r}) \propto \underbrace{e^{-\gamma|\mathbf{R}_{i}-\mathbf{R}_{k}|^{2}}}_{\text{fast decay with}|\mathbf{R}_{i}-\mathbf{R}_{k}|}$$

- For a given $\phi_{\mu}(\mathbf{r})$ only $\phi_{\nu}(\mathbf{r})$ spatially close are non-zero \rightarrow Number of couple non zero $\mu, \nu \propto N_{\mathcal{B}}$ and not to $(N_{\mathcal{B}})^2$
- Therefore for a given couple λ, σ
 - The number of couple non zero $\mu, \nu \propto \textit{N}_{\mathcal{B}}$
 - The number of $(\mu\nu|\lambda\sigma) \neq 0 \propto N_B$
- The total number of non zero $(\mu\nu|\lambda\sigma) \propto (N_B)^2$

The Hartree Fock scaling

Two main steps in Hartree Fock calculation

• Formation of the Fock matrix

$$F_{\mu\nu} = h_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma} [2(\mu\nu|\lambda\sigma) - (\mu\sigma|\lambda\nu)]$$

- $(N_B)^2$ matrix elements each requiring $(N_B)^2$ terms
- Formal scaling as $(N_{\mathcal{B}})^4$
- Diagonalization of $F_{\mu\nu}$
 - Matrix of size N_B
 - Diagonalization is N^3
 - Diagonalization of $F_{\mu
 u}$ scales as $(N_{\mathcal{B}})^3$
- Therefore building $F_{\mu\nu}$ is the main bottleneck of HF
- Formal Hartree-Fock scaling is $(N_{\mathcal{B}})^4$

Exploiting locality and direct SCF

There are two types of SCF algorithms

- Non direct algorithms where you store the $(\mu\nu|\lambda\sigma)$
 - You compute only once the $(\mu
 u | \lambda \sigma)$
 - Memory bottleneck
- Direct algorithms where you don't store the $(\mu\nu|\lambda\sigma)$
 - You compute many times the same $(\mu
 u|\lambda\sigma)$
 - You don't store much

Direct algorithms are the only options for large molecules They made **HF calculations on hundred of atoms feasible**

Exploiting locality in HF calculations

Pre-screening is the key toward large HF calculations

 \bullet discard integrals $(\mu\nu|\lambda\sigma)$ through Schwartz inequality

 $|(\mu\nu|\lambda\sigma)| \le |(\mu\nu|\mu\nu)|^{1/2} |(\lambda\sigma|\lambda\sigma)|^{1/2}$

- If $|(\mu\nu|\mu\nu)|^{1/2}|(\lambda\sigma|\lambda\sigma)|^{1/2} < \eta$, you don't compute it
- Only $(\mu\nu|\mu\nu) = N_{\mathcal{B}}^2$ are to be stored and computed
- For a given $F_{\mu\nu}$, the number of $(\mu\nu|\lambda\sigma) \neq 0 \propto N_B$
- Building all $F_{\mu\nu} \propto (N_B)^3$

• Further **pre-screening** with the **density matrix** $P_{\mu\nu}$

- Because of locality the number of $P_{\mu
 u}
 eq 0 \propto N_{\mathcal{B}}$
- Pre-screening with $P_{\mu\nu}$ leads to an $(N_{\mathcal{B}})^2$ scaling
- Exploiting locality of integrals: $(N_{\mathcal{B}})^4 \rightarrow (N_{\mathcal{B}})^2$

Exploiting locality for correlation methods

- Correlated methods: handle the V_{ii}^{kl} in the MO basis
- MO basis are much more delocalized than the AO basis
- Pre-screening of V_{ij}^{kl} in the MO basis is inefficient
- Need to handle large tensors (ex: T_{ii}^{kl} amplitudes in CC)
- BUT correlation effects are local:
 - Find an alternative basis set for orbital product
 ⇒ Cholesky and density fitting
 - Exploit the locality of correlation for electron pairs
 - \Rightarrow Use of pair natural orbitals
 - \Rightarrow Divide the molecule in domains

Cholesky, density fitting

Decomposition of the two-electron integrals

• Cholesky and density fitting main idea

$$(\mu\nu|\lambda\sigma) = \sum_{P}^{P_{max}} (\mu\nu|P)(P|\lambda\sigma)$$

- $\{P\}$ is an alternative basis set for orbital product
- In a large molecule $P_{max} << N_{\mathcal{B}}^2$
- Then use matrix product with $C_{\mu i}$ to get V_{ij}^{kl}
- Able to handle thousands of basis functions

Pair natural orbitals for CC: main ideas

- Correlation effects are local for a local pair (χ_i, χ_j)
- The CISD wave function for (χ_i, χ_j)

$$|\mathsf{CISD}\rangle_{ij} = |\mathsf{HF}\rangle + \sum_{a} \left(t_i^a a_a^{\dagger} a_i + t_j^a a_a^{\dagger} a_j \right) |\mathsf{HF}\rangle + \sum_{a,b} t_{ij}^{ab} a_a^{\dagger} a_b^{\dagger} a_j a_i |\mathsf{HF}\rangle$$

• Build the natural orbitals of |CISD)

$$D_{mn}^{ij} = \langle \text{CISD}_{ij} | a_m^{\dagger} a_n | \text{CISD}_{ij} \rangle$$
$$D^{ij} = \sum_k n_k^{ij} | \tilde{\chi}_k^{ij} \rangle \langle \tilde{\chi}_k^{ij} |$$

- Natural orbitals are "optimal" for the pair (χ_i, χ_j)
- Then you introduce a threshold on n_k^{ij}
- In practice: don't use the CISD but the $MP^{(1)}$ wave function
- You have to rewrite the CC equation in that basis
- Allows calculations on hundred of electrons

Conclusions

- Calculations post-HF can be done with hundred for large molecules
- Exploit the locality of the basis functions
- Exploit the locality of correlation effects
- I guess it is not going to help in nuclear physics :)