

CHEM 179 / 279 - Numerical Algorithms Applied to Computational Quantum Chemistry

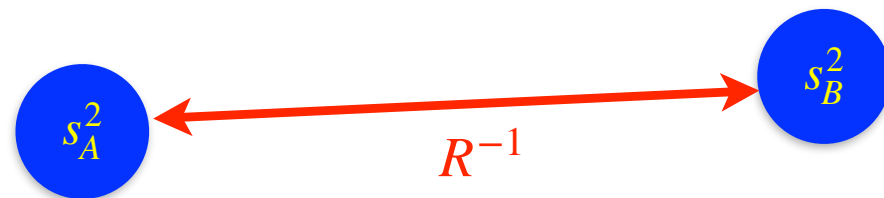
Lecture 20: 3/4/2024

Outline

- Recap and wrap-up: CNDO/2 SCF model
- How to evaluate CNDO/2's two-electron integrals
- CNDO/2 chemistry

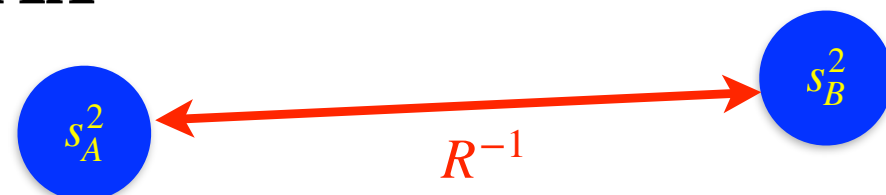
Recap: CNDO/2

- A (quite drastic) simplification of ab initio HF theory
- (i) Use a valence minimal basis (like EHT) so no core 1s electrons for C, N, O, etc.
- (ii) “Zero differential overlap” (ZDO) approximation to simplify 2-electron integrals
 - Like $S_{\mu\nu}$, ERIs decay **exponentially** with distance between ω_μ and ω_ν (& likewise ω_λ and ω_σ)
 - But decay only as R^{-1} with distance between $(\mu\nu)$ and $(\lambda\sigma)$
 - Motivates the ZDO approximation for ERIs: $(\mu\nu | \lambda\sigma) \approx (\mu\mu | \lambda\lambda) \delta_{\mu\nu} \delta_{\lambda\sigma}$
- Approximate retained ERIs so as to preserve rotational invariance of $E_{\text{CNDO/2}}$
 - $(\mu\mu | \lambda\lambda) \leftarrow \gamma_{AB}$ where ω_μ is on atom A, and ω_ν is on atom B
 - $\gamma_{AB} = \int d\mathbf{r} \int d\mathbf{r}' [s_A(\mathbf{r})]^2 |\mathbf{r} - \mathbf{r}'|^{-1} [s_B(\mathbf{r}')]^2$



Recap: CNDO/2 Fock matrix

- $\gamma_{AB} = \int d\mathbf{r} \int d\mathbf{r}' [s_A(\mathbf{r})]^2 |\mathbf{r} - \mathbf{r}'|^{-1} [s_B(\mathbf{r}')]^2$



- Diagonal Fock matrix elements with ZDO

- Each term of the ab initio Hamiltonian is accounted for..... of course with approximations!

- $F_{\mu\mu}^\alpha = -\frac{1}{2} \left(I_\mu + A_\mu \right) + \left[\left(p_{AA}^{\text{tot}} - Z_A \right) - \left(p_{\mu\mu}^\alpha - \frac{1}{2} \right) \right] \gamma_{AA} + \sum_{B \neq A} \left(p_{BB}^{\text{tot}} - Z_B \right) \gamma_{AB}$

Tabulated
IP and EA

On-site
electrostatics

On-site
Exchange

Off-site
electrostatics

- Off-diagonal Fock matrix elements with ZDO

- $F_{\mu\nu}^\alpha = \frac{1}{2} (\beta_A + \beta_B) s_{\mu\nu} - p_{\mu\nu}^\alpha \gamma_{AB}$

Tabulated
site-site
h+J

site-site
exchange

quantity	H	C	N	O	F
$\frac{1}{2} (I_s + A_s)$	7.176	14.051	19.316	25.390	32.272
$\frac{1}{2} (I_p + A_p)$		5.572	7.275	9.111	11.080
$-\beta$	9	21	25	31	39

(eV)

CNDO/2 SCF method

- The CNDO/2 method applies the ZDO approximation to the overlap matrix also
 - As a consequence, the eigenvalue problem is conventional (like Huckel) not generalized (like EHT & HF)
 - For unrestricted orbitals, we have the following equations for the unknown MO coefficients.
 - $\mathbf{F}^\alpha \mathbf{C}^\alpha = \mathbf{C}^\alpha \boldsymbol{\epsilon}^\alpha$ $\mathbf{F}^\beta \mathbf{C}^\beta = \mathbf{C}^\beta \boldsymbol{\epsilon}^\beta$
- The density matrices needed to build the Fock matrices are given by:
 - $P_{\mu\nu}^\alpha = \sum_i^p C_{\mu i}^\alpha C_{\nu i}^\alpha$ $P_{\mu\nu}^\beta = \sum_i^q C_{\mu i}^\beta C_{\nu i}^\beta$ $P_{AA}^{\text{tot}} = \sum_{\mu \in A} [P_{\mu\mu}^\alpha + P_{\mu\mu}^\beta]$
- The Fock matrix expressions also involve:
 - The tabulated parameters (easy to implement): β_μ , I_μ , A_μ
 - The (geometry-dependent) overlap matrix: Ready to re-use from your EHT code
 - The small number of ERIs. We must discuss how to evaluate them!

Evaluation of 2-electron integrals

- Let's look closely at the 2-center, 2-electron integrals:

- $$\gamma_{AB} = \int d\mathbf{r}_1 \int d\mathbf{r}_2 [s_A(\mathbf{r}_1)]^2 |\mathbf{r}_1 - \mathbf{r}_2|^{-1} [s_B(\mathbf{r}_2)]^2$$

- The atomic spherical charge distributions are defined as

- $$s_A(\mathbf{r}) \equiv \sum_k^3 \left(d_{ks_A} N_k^s \right) \omega_k^s(\mathbf{r} - \mathbf{R}_A) = \sum_k^3 d'_{ks_A} \omega_k^s(\mathbf{r} - \mathbf{R}_A)$$

contraction
coefficient

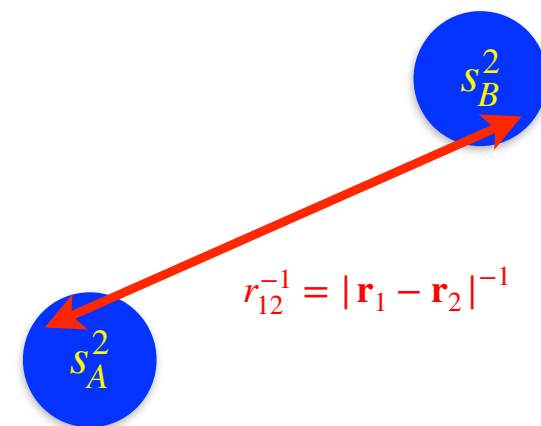
normalization

primitive s-type
Gaussian

- Expanding it out gives 81 primitive contributions

- $$\gamma_{AB} = \sum_k^3 \sum_{k'}^3 \sum_l^3 \sum_{l'}^3 d'_{ks_A} d'_{k's_A} d'_{ls_B} d'_{l's_B} [0]^{(0)}$$

- $$[0]^{(0)} = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \omega_k^s(\mathbf{r}_1 - \mathbf{R}_A) \omega_{k'}^s(\mathbf{r}_1 - \mathbf{R}_A) \frac{1}{r_{12}} \omega_l^s(\mathbf{r}_2 - \mathbf{R}_B) \omega_{l'}^s(\mathbf{r}_2 - \mathbf{R}_B)$$



Evaluation of 2-electron integrals

- Key result: this difficult-looking 6D integral can be reduced to a 1D integral
 - As first proven by S.F. Boys in 1950 (the integral is called the Boys function)
 - $[0]^{(0)} = U_A U_B \sqrt{2V^2} \sqrt{\frac{2}{\pi}} \int_0^1 \exp(-Tu^2) du$
- The constants T , U_A , U_B , V are all related to the Gaussian exponents and positions:
 - $T = V^2 (\mathbf{R}_A - \mathbf{R}_B)^2$
 - $V^2 = (\sigma_A + \sigma_B)^{-1}$
 - $U_A = (\pi\sigma_A)^{3/2}$
 - $\sigma_A = (\alpha_k + \alpha_{k'})^{-1}$

The Boys function is an error function

- Here is the key identity
 - $\int_0^1 \exp(-Tu^2) du = \frac{1}{2} \sqrt{\frac{\pi}{T}} \operatorname{erf}(\sqrt{T})$
- The error function varies from 0 (as $x \rightarrow 0$) to 1 (as $x \rightarrow \infty$):
 - $\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-v^2) dv$
- In fact, electron repulsion does not diverge as $|\mathbf{R}_A - \mathbf{R}_B| \rightarrow 0$
 - $\lim_{r \rightarrow 0} [r^{-1} \operatorname{erf}(r)] = 2/\sqrt{\pi}$
 - A consequence of charge distributions rather than point charges!

Notes on this evaluation

- This method of computing the s-type 2-center, 2-electron integrals is both efficient and accurate
 - You have already gone over things related to this in your lab section this week
- Algorithms for evaluating erf are in Numerical Recipes Ch. 6.2, but also it's a function call available in Armadillo
- Physically, we consider the net charge on an atom to be spherical and compute the Coulomb repulsion of that amount of net charge from the other spherical net charges

Converging SCF equations

- SCF equations are non-linear
 - There are no formal guarantees that the SCF procedure will converge
 - Depends on initial guess
- We discussed $P=0$ as a guess last week, but that's not a very good guess!
 - Only works for very well-behaved molecules
- Another convenient alternative is a Hückel guess (you will have all the pieces)
 - Form $H_{\mu\mu} = -\frac{1}{2} (I_{\mu} + A_{\mu})$, $H_{\mu\nu} = -\frac{1}{2}(\beta_A + \beta_B)S_{\mu\nu}$
 - Solve $\mathbf{H}\mathbf{C}^{(0)} = \mathbf{C}^{(0)}\epsilon$
 - Make $(P^{\beta}_{\mu\nu})^{(0)} = \sum_i^q C_{\mu i}^{(0)} C_{\nu i}^{(0)}$; $(P^{\alpha}_{\mu\nu})^{(0)} = \sum_i^p C_{\mu i}^{(0)} C_{\nu i}^{(0)}$

CNDO/2 chemistry: diatomic molecules

Molecule	Equilibrium bond length (Å)		Binding energy (eV)	
	CNDO/2	Experiment	CNDO/2	Experiment
H ₂	0.75	0.74	5.4	4.8
HB	1.19	1.23	10.0	3.6
HF	1.00	0.92	6.8	6.1
CO	1.19	1.13	22.2	11.2
N ₂	1.14	1.09	25.5	9.9
OH	1.03	0.97	7.4	4.6
CH	1.11	1.12	9.6	3.6
CN	1.17	1.17	23.8	7.6

Far better than EHF
(Less good than HF)

Drastically poorer than HF
(Huge overbinding)