Electron correlation *versus* electron-nucleus correlation

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Outline

- How to define electron-nucleus correlation?

By analogy with electronic correlation energy

- How to calculate electron-nucleus correlation?

The electron-nucleus mean field configuration interaction (EN-MFCI) method.

- How to understand some case example results?

How about a Quantum Chemistry without Born-Oppenheimer?

1. How to define EN-correlation?

Independence ($\Leftrightarrow$ no correlation) in probability theory

- $p(A \text{ and } B) = p(A) \cdot p(B)$

Born probabilistic interpretation of the wave function

- $|\psi(r)|^2 = p(r)$: probability of being observed at point r.

Distinguishable particles: Hartree product ($\psi_H = \psi_1 \otimes \psi_2$)

- $\psi_H(r_1, r_2) = \psi_1(r_1)\psi_2(r_2) \Rightarrow |\psi_H(r_1, r_2)|^2 = |\psi_1(r_1)|^2 \, |\psi_2(r_2)|^2$

Fermionic particles: Slater determinant ($\psi_S = \psi_1 \wedge \psi_2$)

- $\psi_S(r_1, r_2) = \frac{\psi_1(r_1)\psi_2(r_2) - \psi_1(r_2)\psi_2(r_1)}{\sqrt{2}} \Rightarrow |\psi_S(r_1, r_2)|^2 \neq |\psi_1(r_1)|^2 \, |\psi_2(r_2)|^2$

$\rightsquigarrow$ some correlation but just spin statistic correlation

Electronic correlation energy in quantum chemistry

$$E^{el}_{correl} = \overset{Min}{\psi_S} \langle \psi_S | H | \psi_S \rangle - \langle \psi_{FullCI} | H | \psi_{FullCI} \rangle$$

$$\Leftrightarrow$$

$$E^{el}_{correl} = \langle \psi_{HF} | H | \psi_{HF} \rangle - \langle \psi_{FullCI} | H | \psi_{FullCI} \rangle$$

$\rightsquigarrow$ Electron-nucleus correlation energy

$\psi_H(\vec{R}^n, \vec{R}^e) = \psi_n(\vec{R}^n)\psi_e(\vec{R}^e)$

$$E^{EN}_{correl} = \overset{Min}{\psi_H} \langle \psi_H | H | \psi_H \rangle - \langle \psi_{FullCI} | H | \psi_{FullCI} \rangle$$

$$\Leftrightarrow$$

$$E^{EN}_{correl} = \langle \psi_{EN-SCFCI} | H | \psi_{EN-SCFCI} \rangle - \langle \psi_{FullCI} | H | \psi_{FullCI} \rangle$$

$\rightsquigarrow$ Born-Oppenheimer ansatz has built-in EN-correlation

$\psi_{BO}(\vec{R}^n, \vec{R}^e) = \psi_n(\vec{R}^n)\psi_e(\vec{R}^n, \vec{R}^e)$ with $|\psi_e(\vec{R}^n, \vec{R}^e)|^2 \neq |\psi_1(\vec{R}^n)|^2 \, |\psi_2(\vec{R}^e)|^2$

2. How to calculate EN-correlation?

Notation

- $\vec{R}^e := (\vec{r}_1{}^e, \vec{r}_2{}^e, \ldots, \vec{r}_p{}^e)$: electronic position variables
- $\vec{R}^n := (\vec{r}_1{}^n, \vec{r}_2{}^n, \ldots, \vec{r}_N{}^n)$: nuclear position variables
- $\vec{Q} := (Q_1, Q_2, \ldots, Q_q)$: mass-weighted normal coordinates.
- $\Delta\vec{R}^n = \vec{R}^n - \vec{R}^0$: Cartesian displacements

- $\hat{G}$: $(3N \times 3N)$ diagonal matrix of the square roots of nuclear masses
- $\hat{L}$: $(q \times 3N)$ orthogonal matrix such that $\vec{Q} = \hat{L}\hat{G}\Delta\vec{R}^n$
- $\hat{G}_a^{-1}$: $(3 \times 3N)$ submatrix of $\hat{G}^{-1}$ corresponding to nucleus a

with these notation $\vec{r}_a{}^n = \hat{G}_a^{-1}\hat{L}^T\vec{Q} + \vec{r}_a{}^0$ when $rotation = translation = 0$

- $\hat{H}(\vec{R}^e) = -\frac{1}{2\mu_e}\sum_{i=1}^{p}\Delta_{\vec{r}_i^e} + \sum_{1\le i<j\le p}\frac{1}{\|\vec{r}_i{}^e - \vec{r}_j{}^e\|}$: electronic Hamiltonian
- $\hat{H}(\vec{Q}) = -\frac{1}{2}\sum_{i=1}^{q}\Delta_{Q_i} + \sum_{1\le a<b\le N}\frac{Z_aZ_b}{\|\vec{r}_a{}^0 - \vec{r}_b{}^0 + \hat{G}_a^{-1}\hat{L}^T\vec{Q} - \hat{G}_b^{-1}\hat{L}^T\vec{Q}\|}$: nuclear Hamiltonian
- $\hat{H}(\vec{R}^e, \vec{Q}) = -\sum_{i=1}^{p}\sum_{a=1}^{N}\frac{Z_a}{\|\vec{r}_i{}^e - \vec{r}_a{}^0 - \hat{G}_a^{-1}\hat{L}^T\vec{Q}\|}$: electron-nucleus coupling

Electron-Nucleus MFCI: principle

1 • Start from an effective electronic Hamiltonian

$$\hat{H}^{eff}(\vec{R}^e) = \hat{H}(\vec{R}^e) + \langle \phi_{\vec{0}}^{(0)}(\vec{Q}) | \hat{H}(\vec{Q}) + \hat{H}(\vec{R}^e, \vec{Q}) | \phi_{\vec{0}}^{(0)}(\vec{Q}) \rangle_{\vec{Q}}$$

⋆ $\phi_{\vec{0}}^{(0)}(\vec{Q}) = \delta(\vec{Q}_0)$ ↦ clamped nuclei approximation

⋆ $\phi_{\vec{0}}^{(0)}(\vec{Q})$ = GS of a Kratzer potential $D\left(\frac{Q}{Q+\xi_{ab}^0}\right)^2$ ↦ vibrationally averaged $\hat{H}^{eff}(\vec{R}^e)$

⇝ Obtain a basis set of electronic approximate eigenstates $\psi_i(\vec{R}^e)$ (not $\psi_i(\vec{R}^e, Q)$ like in BO)

2 • Keep electrons and nuclei uncontracted?

YES ⇝ **set $\phi_0^{(1)}(\vec{R}^e) = \psi_0(\vec{R}^e)$ and solve an effective vibrational Hamiltonian**

$$\hat{H}^{eff}(\vec{Q}) = \hat{H}(\vec{Q}) + \langle \phi_0^{(1)}(\vec{R}^e) | \hat{H}(\vec{R}^e) + \hat{H}(\vec{R}^e, \vec{Q}) | \phi_0^{(1)}(\vec{R}^e) \rangle_{\vec{R}^e}$$

and loop back to 1

Remark: $\langle \phi_0^{(1)}(\vec{R}^e) | \hat{H}(\vec{R}^e, \vec{Q}) | \phi_0^{(1)}(\vec{R}^e) \rangle_{\vec{R}^e}$ known analytically, but integrals calculated directly.

Electron-Nucleus SCFCI: convergence

Setting $H_{Coulomb} = \hat{H}(\vec{Q}) + \hat{H}(\vec{R}^e) + \hat{H}(\vec{R}^e, \vec{Q})$,

$$\langle \phi_{\vec{0}}^{(n)} \phi_0^{(n+1)} | H_{Coulomb} | \phi_{\vec{0}}^{(n)} \phi_0^{(n+1)} \rangle = \langle \phi_0^{(n+1)} | \hat{H}^{eff^{(n)}} | \phi_0^{(n+1)} \rangle_{\vec{R}^e}$$

If $\hat{H}^{eff^{(n)}} \psi = E\psi$ is solved variationally and if the variational space includes $\phi_0^{(n-1)}$ then

$$\langle \phi_0^{(n+1)} | \hat{H}^{eff^{(n)}} | \phi_0^{(n+1)} \rangle_{\vec{R}^e} \leq \langle \phi_0^{(n-1)} | \hat{H}^{eff^{(n)}} | \phi_0^{(n-1)} \rangle_{\vec{R}^e}$$

hence

$$\cdots \leq \langle \phi_{\vec{0}}^{(n)} \phi_0^{(n+1)} | H_{Coulomb} | \phi_{\vec{0}}^{(n)} \phi_0^{(n+1)} \rangle \leq \langle \phi_0^{(n-1)} \phi_{\vec{0}}^{(n)} | H_{Coulomb} | \phi_0^{(n-1)} \phi_{\vec{0}}^{(n)} \rangle \leq \cdots$$

iteration nb	HF	Full CI
0	-1.11 00467	-1.15 08083
1	-1.113 8025	-1.154 6101
2	-1.113 9342	-1.154 7108
3	-1.1139 687	-1.1547 212
4	-1.1139 925	-1.1547 273
5	-1.1140 094	-1.15473 17
6	-1.1140 215	-1.15473 49
7	-1.1140 300	-1.15473 74
⋮	⋮	⋮

H_2 total energy in hartree

[cc-pV5Z + 16 (2s)] ⊗ [16 Kratzer] basis.

Variational space: $V = V_{FullCI}^{vib} \otimes V_{FullCI}^{elec}$

⇝ best wave function of the form:

$\psi_H = \psi_n \otimes \psi_e$

and:

$E_{EN-SCFCI} = \langle \psi_{EN-SCFCI} | H | \psi_{EN-SCFCI} \rangle$

Electron-Nucleus CI

2 • Keep electrons and nuclei uncontracted?

$NO \rightsquigarrow$ **Electron-Nuclei CI in direct product basis set :**

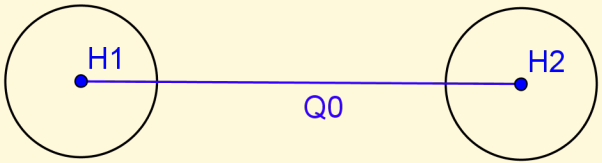
$$\{\psi_j(Q)\psi_i(\vec{R}^e)\}_{(j,i)}$$

In particular, $\rightsquigarrow$ **Electron-Nuclei Full CI**

$$\rightsquigarrow \quad E_{EN-FullCI} = \langle\psi_{FullCI}|H|\psi_{FullCI}\rangle$$

Electron-Nucleus MFCI: basis set pb

$\rightsquigarrow$ Core atomic orbitals unsuited to describe vibrationally averaged molecular electronic clouds:



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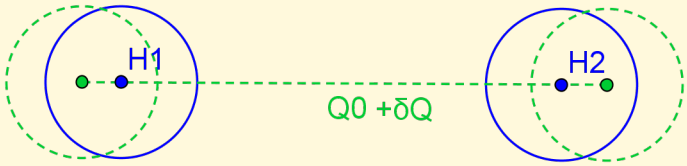

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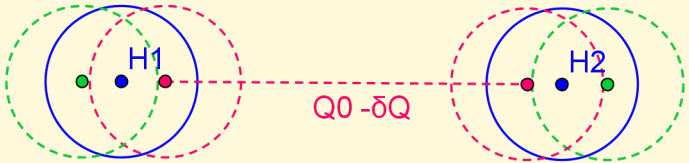

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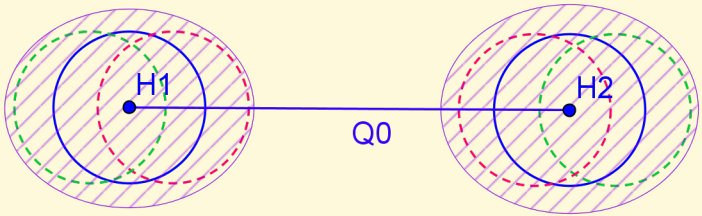

Electron-Nucleus Full CI results

H_2

Transition	TF-NOMO/CIS	TF-NOMO/FCI	this work	Exp.
$\nu: 0 \to 1$	4655	4182	4165	4161
$\nu: 0 \to 2$	9406	N/A	8110	8087
$\Sigma_g^+: 0 \to 1$	106556	N/A	91711	91700

D_2

Transition	TF-NOMO/CIS	TF-NOMO/FCI	this work	Exp.
$\nu: 0 \to 1$	3549	3006	2994	2994
$\nu: 0 \to 2$	7026	N/A	5874	5869
$\Sigma_g^+: 0 \to 1$	107628	N/A	92182	91697

T_2

Transition	TF-NOMO/CIS	TF-NOMO/FCI	this work	Exp.
$\nu: 0 \to 1$	2929	2477	2465	2465
$\nu: 0 \to 2$	5843	N/A	4851	4849
$\Sigma_g^+: 0 \to 1$	108043	N/A	92375	91696

Vibrational and electronic transition wave numbers (in cm^{-1})

from H. Nakai Int. J. Quantum Chem. **107**, 2849 (2007). Except "This work":
P. Cassam-Chenaï, B. Suo, W. Liu, Phys. Rev. **A92**, 012502 (2015).

3. How to understand some case example results?

Convergence of ground state energy with MFCI iterations

	H_2		D_2		T_2	
iteration number	HF	Full CI	HF	Full CI	HF	Full CI
0	-1.1100467	-1.1508083	-1.1167995	-1.1575238	-1.1198084	-1.1605164
1	-1.1138025	-1.1546101	-1.1195670	-1.1603205	-1.1221191	-1.1628484
2	-1.1139342	-1.1547108	-1.1196533	-1.1603841	-1.1221867	-1.1628971
3	-1.1139687	-1.1547212	-1.1196775	-1.1603892	-1.1222067	-1.1629007
4	-1.1139925	-1.1547273	-1.1196943	-1.1603926	-1.1222208	-1.1629030
5	-1.1140094	-1.1547317	-1.1197066	-1.1603949	-1.1222308	-1.1629043
6	-1.1140215	-1.1547349	-1.1197148	-1.1603967	-1.1222379	-1.1629055
7	-1.1140300	-1.1547374	-1.1197209	-1.1603978	-1.1222430	-1.1629067
8	-1.1140360	-1.1547391	-1.1197252	-1.1603988	-1.1222467	-1.1629073
9	-1.1140404	-1.1547403	-1.1197283	-1.1603993	-1.1222493	-1.1629076
CV	-1.1140507	-1.1547436	-1.1197358	-1.1604013	-1.1222556	-1.1629091
EN-FullCI	-1.1638438		-1.1669493		-1.1683018	

$E^{el}_{correl} = E^{(0)}_{HF} - E^{(0)}_{FullCI}$ $\quad E^{MF}_{scf} = E^{(0)}_{FullCI} - E^{(CV)}_{FullCI}$ $\quad E^{EN}_{correl} = E^{(CV)}_{FullCI} - E^{EN}_{FullCI}$

Correlation energies for hydrogen isotopologues

E^{el}_{correl}=$E^{(0)}_{HF}$-$E^{(0)}_{FullCI}$ $\quad$ E^{MF}_{scf} = $E^{(0)}_{FullCI}$-$E_{EN-SCFCI}$ $\quad$ E^{EN}_{correl} = $E_{EN-SCFCI}$-E^{EN}_{FullCI}

Correlation energies (hartrees)

	$\mathbf{H_2}$	$\mathbf{D_2}$	$\mathbf{T_2}$
E^{el}_{correl}	.0407616	.0407243	.0407080
E^{MF}_{scf}	.0039353	.0028775	.0023927
E^{EN}_{correl}	.0091002	.0065480	.0053927

How about a Quantum Chemistry without Born-Oppenheimer?

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The Wave Mechanics of an Atom with a Non-Coulomb Central Field. Part I. Theory and Methods. By D. R. HARTREE, Ph.D., St John's College.

[*Received* 19 November, *read* 21 November, 1927.]

§ 1. *Introduction.*

On the theory of atomic structure proposed by Bohr, in which the electrons are considered as point charges revolving in orbits about the nucleus, the orbits being specified by quantum conditions, it is well known that both a qualitative and an approximate quantitative explanation of many features of the simpler optical spectra and of X-ray spectra of atoms with many electrons (e.g. Rydberg sequences in optical spectra, term magnitudes in both X-ray and optical spectra) can be given, if the assumption is made that the effects of the electrons on one another can be represented by supposing each to move in a central non-Coulomb field of force*; further, the additional concept of a spinning electron provides a similar explanation of other features of these spectra† (e.g. doublet structure of terms and magnitude of doublet separation, anomalous Zeeman effect). This assumption of a central field was admittedly a rough approximation made in the absence of any detailed ideas about the interaction between the different electrons in an atom, but in view of its success as a first approximation for the orbital atom model, the question arises whether the same simple approximations may not give useful results when applied to the new formulation of the quantum theory which has been developed in the last two years.

The wave mechanics of Schrödinger‡ appears to be the most suitable form of the new quantum theory to use for this purpose, and will be adopted throughout. Further, if ψ is a solution of the wave equation (suitably normalised), the suggestion has been made by Schrödinger, and developed by Klein§, that $|\psi|^2$ gives the volume density of charge in the state described by this ψ; whether this interpretation is always applicable may be doubtful, but for the wave functions corresponding to closed orbits of electrons in an atom, with which alone this paper will be concerned, it has the advantage that it gives something of a model both of the stationary states (if ψ only contains one of the characteristic functions) and of the process of radiation (if ψ is the sum of

* See, for example, M. Born, *Vorlesungen über Atommechanik* (or the English translation, *The Mechanics of the Atom*), Ch. III.

† For a general review, see R. H. Fowler, *Nature*, Vol. CXIX, p. 90 (1927); for a more detailed treatment, F. Hund, *Linienspektren*, Ch. III.

‡ E. Schrödinger, *Ann. der Phys.*, Vol. LXXIX, pp. 361, 489; Vol. LXXX, p. 437; Vol. LXXXI, p. 109 (1926); *Phys. Rev.*, Vol. XXVIII, p. 1049 (1926).

§ F. Klein, *Zeit. f. Phys.*, Vol. XLI, p. 432 (1927).

Selected rotational energy levels (in cm^{-1}) of H_2

	this work	Pachucki et al. 2009	Matyus et al. 2012
$\underline{\nu = \mathbf{0}}$			
$J = 1$	118.4	118.4851	118.485355
$J = 2$	354.1	354.3684	354.369007
$J = 3$	705.1	705.5097	705.509982
$J = 4$	1168.1	1168.7825	1168.782740
$J = 5$	1739.1	1740.1675	N/A
$J = 14$	10797.7	10800.9043	N/A
$\underline{\nu = \mathbf{1}}$			
$J = 1$	112.5	112.5730	N/A
$J = 2$	336.5	336.6682	N/A
$J = 3$	669.9	670.2172	N/A
$J = 4$	1109.7	1110.2000	N/A
$J = 5$	1652.2	1652.7361	N/A
$J = 14$	10257.8	10237.9613	N/A
$\underline{\nu = \mathbf{2}}$			
$J = 1$	107.0	106.7905	N/A
$J = 2$	319.9	319.3545	N/A
$J = 3$	637.0	635.6922	N/A
$J = 4$	1055.6	1052.8833	N/A
$J = 5$	1572.0	1567.1775	N/A
$J = 14$	9795.1	9684.4911	N/A
$\underline{\nu = \mathbf{5}}$			
$J = 1$	88.3	89.7800	N/A
$J = 2$	264.5	268.4120	N/A
$J = 3$	527.8	534.0707	N/A
$J = 4$	876.7	884.0925	N/A
$J = 5$	1309.0	1168.7825	N/A
$J = 14$	8218.6	8029.4047	N/A

Comparison of full and limited electron-nucleus CI calculations

	Full CI	Limited CI
Number of CSF's	144720	6286
E^0 (hartrees)	−1.1638438	−1.1638413
$\nu:\ 0 \rightarrow 1$ (cm^{-1})	4165.36	4165.86

The configuration state functions (CSF's) selected for the limited CI were those having a coefficient in the full CI expansion of the ground or first excited states with absolute value larger than 10^{-5}.