

The nitty-gritty of explicitly correlated wave functions for the calculation of electric properties

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How do we calculate electric properties?

1. Expectation value

$$\langle \hat{\Omega} \rangle_{\psi} = \langle \psi | \hat{\Omega} | \psi \rangle, \quad (1)$$

where $\hat{\Omega} \in \{\mu, \alpha\}$ for our purposes.

2. Energy derivatives, analytically or numerically

$$E = E_0 + \left(\frac{\partial E}{\partial \mathbf{F}} \right)_{\mathbf{F}=0} \mathbf{F} + \frac{1}{2} \mathbf{F}^t \left(\frac{\partial^2 E}{\partial \mathbf{F}^2} \right)_{\mathbf{F}=0} \mathbf{F} + \dots \quad (2)$$

Response theory: compare equ. (2) with

$$E = E_0 - \mu \mathbf{F} - \frac{1}{2} \mathbf{F}^t \alpha \mathbf{F} - \dots \quad (3)$$

Thus, in terms of finite differences we can write

$$\mu = - \left(\frac{\partial E}{\partial \mathbf{F}} \right)_{\mathbf{F}=\mathbf{0}} \quad (4)$$

$$\approx \frac{E(\mathbf{F} = \mathbf{0}) - E(\mathbf{F} = \boldsymbol{\varepsilon})}{\boldsymbol{\varepsilon}} \quad (5)$$

and

$$\alpha = - \left(\frac{\partial^2 E}{\partial \mathbf{F}^2} \right)_{\mathbf{F}=\mathbf{0}} \quad (6)$$

$$\approx \frac{-E(\mathbf{F} = \boldsymbol{\varepsilon}) + 2E(\mathbf{F} = \mathbf{0}) - E(\mathbf{F} = -\boldsymbol{\varepsilon})}{\boldsymbol{\varepsilon}^2} . \quad (7)$$

Need

$$E(\mathbf{F} = \boldsymbol{\varepsilon}) = \langle \hat{T} \rangle + \langle \hat{V} \rangle + \boldsymbol{\varepsilon} \langle \hat{f} \rangle \quad (8)$$

How do we get $\langle \hat{f} \rangle$?

Easy! $\hat{f} = \sum_i q_i \hat{\mathbf{r}}_i$, which requires integrals of type $\langle \phi | \mathbf{r} | \phi \rangle$ in a given one-electron basis $\{|\phi_i\rangle\}_{i=1}^n$.

Problem: convergence of the correlation energy $E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}}$ with one-electron basis is very slow — known to behave as $\sim (l + \frac{1}{2})^{-4}$ with respect to angular quantum number l in atoms.

	ΔSCF	Δcorr	% corr
cc-pVDZ	58	136	58%
cc-pVTZ	15	56	83%
cc-pVQZ	3.5	26	92%
cc-pV5Z	0.2	14	96%
Total	-128.54709 E_h	-320.2	

Table 1: Ne atom energies using correlation consistent basis sets (mE_h) taken from B. J. Persson and P. R. Taylor, J. Chem. Phys. **105**, 5915, (1996)

- ▶ In a helium atom, $\lim_{r_{12} \rightarrow 0} \psi = 1 + \frac{1}{2}r_{12}$.
- ▶ Dynamical correlation arises from the behaviour of the wave function as two electrons approach one another, cusp required to cancel r_{ij}^{-1} singularity. Wave function should be linear in the region of the correlation cusp.
- ▶ Trying to describe a two-electron cusp in terms of one-electron functions.

Include functions that depend explicitly on coordinates of two electrons rather than just one, e. g. in Gaussian type geminals (GTGs)

$g(a, b, c, d, e, f, \alpha, \beta, \gamma, \mathbf{A}, \mathbf{B})$

$$\begin{aligned}
 g &= x_i^a x_i^b y_i^c y_j^d z_j^e z_j^f \exp\left(-\alpha r_{iA}^2 - \beta r_{jB}^2 - \gamma r_{ij}^2\right) \\
 &= \phi_i(a, b, c, \alpha, \mathbf{A}) \phi_j(d, e, f, \beta, \mathbf{B}) \underbrace{\exp\left(-\gamma r_{ij}^2\right)}_{\text{GCF } f(\gamma, r_{ij})} \quad (9)
 \end{aligned}$$

However, GTGs lack the correct cusp behaviour. → Mimic linear r_{ij} by expansion

$$r_{ij} = 1 + \lim_{n \rightarrow \infty} \sum_k^n c_k \exp\left(-\gamma_k r_{ij}^2\right) \quad (10)$$

- ▶ Cannot describe cusp exactly, but experience shows much better convergence in terms of the energy than one-electron bases.
- ▶ Can obtain over 90% of the correlation energy by adding six correlation factors to a cc-pVDZ basis (as good as or better than cc-pVQZ!), and 99% by adding six correlation factors to a cc-pVTZ basis.

What are the consequences for $\langle \hat{f} \rangle$?

Not so easy anymore. . .

Now we need two-electron integrals of type

$$\langle g(\gamma_v, r_{12}) \phi_i \phi_{i'} | \mathbf{r}_1 + \mathbf{r}_2 | \phi_j \phi_{j'} \rangle, \quad \gamma_v \in \mathbb{R} \quad (11)$$

and

$$\langle g(\gamma_v, r_{12}) \phi_i \phi_{i'} | \mathbf{r}_1 + \mathbf{r}_2 | g(\gamma_w, r_{12}) \phi_j \phi_{j'} \rangle \quad \gamma_v, \gamma_w \in \mathbb{R} \quad (12)$$

First, a few definitions:

We consider GTOs of the Cartesian form

$$G_{ijk}(\mathbf{r}, a, \mathbf{A}) \stackrel{\text{def}}{=} x_A^i y_A^j z_A^k \exp\left(-ar_A^2\right). \quad (13)$$

GTOs commonly appear in pairs as an overlap distribution

$$\Omega_{il,jm,kn}(\mathbf{r}, a, b, \mathbf{A}, \mathbf{B}) \stackrel{\text{def}}{=} G_{ijk}(\mathbf{r}, a, \mathbf{A}) G_{lmn}(\mathbf{r}, b, \mathbf{B}) . \quad (14)$$

The benefits are obvious:

- ▶ Factorization into three Cartesian components is obtained straightforwardly
- ▶ Recursion formulas are readily available
- ▶ The product of two exponentials may be rewritten as a single factor using the Gaussian product rule

By introducing Hermite Gaussian functions

$$\Lambda_{tuv}(\mathbf{r}, p, \mathbf{P}) \stackrel{\text{def}}{=} \left(\frac{\partial}{\partial P_x} \right)^t \left(\frac{\partial}{\partial P_y} \right)^u \left(\frac{\partial}{\partial P_z} \right)^v \exp \left(-pr_P^2 \right) \quad (15)$$

we can expand the overlap distribution as

$$\Omega_{il,jm,kn} = \sum_{t=0}^{i+l} \sum_{u=0}^{j+m} \sum_{v=0}^{k+n} E_t^{il} E_u^{jm} E_v^{kn} \Lambda_{tuv} \quad (16)$$

$$= \sum_{tuv} E_{tuv} \Lambda_{tuv} . \quad (17)$$

Well, how do we get $\langle \hat{f} \rangle$ now?

We start from the two-electron overlap integrals

$$I_{\text{ovl}} = I_x I_y I_z \quad (18)$$

involving one geminal, i. e.

$$\langle \exp(-\gamma_v r_{12}^2) \phi_i \phi_{i'} | \phi_j \phi_{j'} \rangle . \quad (19)$$

When we wish to calculate the energy of a system with an electric field in, say, the x -direction, the integrals to be evaluated are of type $D_x I_y I_z$.

The overlap integral is evaluated as

$$\begin{aligned} & \iint d^2\mathbf{r} \exp(-\gamma_v r_{12}^2) \phi_i(1) \phi_{i'}(2) \phi_j(1) \phi_{j'}(2) \\ = & \iint d^2\mathbf{r} \exp(-\gamma_v r_{12}^2) \Omega_{ij}(1) \Omega_{i'j'}(2) \end{aligned} \quad (20)$$

$$= \sum_{tuv} E_{tuv}^{ij} \sum_{t'u'v'} E_{t'u'v'}^{i'j'} V_{tuv;t'u'v'} \quad (21)$$

with the Hermite integrals

$$V_{tuv;t'u'v'} = V_{t;t'}^x V_{u;u'}^y V_{v;v'}^z, \quad (22)$$

where the x -direction, for example, is given by

$$V_{t;t'}^x = \frac{\pi}{\sqrt{pp' + \gamma_v(p + p')}} (-1)^t \left(\frac{\partial}{\partial P_x} \right)^{t+t'} \exp(-aX_{PP'}^2). \quad (23)$$

That is excellent! This means, that we only have to do $1/3$ of the work, i. e. the evaluation of D_x in our case.

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$$\begin{aligned}
 \langle \hat{f} \rangle = & \left(\sum_{t=0}^{i+j+1} \sum_{t'=0}^{i'+j'} E_t^{i+1,j} E_{t'}^{i',j'} V_{t;t'}^x + \sum_{t=0}^{i+j} \sum_{t'=0}^{i'+j'+1} E_t^{i,j} E_{t'}^{i'+1,j'} V_{t;t'}^x \right. \\
 & \left. + (X_A + X_C - X_{PE} - X_{P'E}) \sum_{t=0}^{i+j} \sum_{t'=0}^{i'+j'} E_t^{i,j} E_{t'}^{i',j'} V_{t;t'}^x \right) \\
 & \sum_{u=0}^{k+l} \sum_{u'=0}^{k'+l'} E_u^{k,l} E_{u'}^{k',l'} V_{u;u'}^y \sum_{v=0}^{m+n} \sum_{v'=0}^{m'+n'} E_v^{m,n} E_{v'}^{m',n'} V_{v;v'}^z . \quad (24)
 \end{aligned}$$

And some time later, after a little programming effort has been made, we eventually obtain. . .

Selected results

GCFs	α
0/0.0/0.0	1.360
1/1.0/1.0	1.360
2/1.0/3.0	1.353
2/2.0/3.0	1.358
3/1.0/3.0	1.355
3/3.0/3.0	1.363
4/1.0/2.0	1.352
4/9.0/3.0	1.353
5/1.0/2.0	1.382
5/9.0/3.0	1.352
6/1.0/2.0	1.387
6/27.0/3.0	1.350
FCI	1.383

Table 2: Polarizabilities for helium, aug-cc-pVQZ

GCFs	α
0/0.0/0.0	42.23
1/1.0/1.0	41.93
2/1.0/3.0	41.84
3/1.0/3.0	41.64
4/1.0/2.0	41.50
5/1.0/2.0	41.46
6/1.0/2.0	41.70
MCSCF	37.73
MRCI	37.82
MRCI+Q	37.95
AQCC	37.85

Table 3: Polarizabilities for beryllium, 6-311++G(3*df*,3*pd*)

GCFs	α_{\parallel}	α_{\perp}	μ
0/0.0/0.0	6.428	5.299	0.714
1/1.0/1.0	6.771	5.300	0.710
3/3.0/3.0	6.865	5.232	0.722
6/27.0/3.0	9.700	5.214	0.727
MCSCF	6.286	5.163	0.721
MRCI	6.397	5.221	0.709
MRCI+Q	6.433	5.265	0.708
AQCC	6.311	5.238	0.708

Table 4: Polarizabilities for hydrogen fluoride, d-aug-cc-pVDZ (MP2-GTG) and d-aug-cc-pVTZ (benchmarks)

High dependence on GCFs!

Summary

- ▶ GCFs to augment conventional orbital basis sets gives substantially improved correlation energies
- ▶ Addition of geminals to the wave function is capable of improving the description of electric properties, as it is the case for beryllium
- ▶ Such improvements cannot be expected to be universal
- ▶ Better correlation energy does not necessarily imply improved description of electric properties

Discussion