

Variational Reduced Density Matrix Theory: Successes and Failures

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Generalized Density Functional Theories: Going past the density, but not yet to the wave function

$$\gamma(r, r') \quad \Gamma_2(r_1, r_2; r'_1, r'_2) \quad \Gamma_3(r_1, r_2, r_3; r'_1, r'_2, r'_3) \quad \Gamma_4$$

$$\rho(r) \quad \rho_2(r, r') \quad \rho_3(r_1, r_2, r_3) \quad \rho_4(r_1, \dots, r_4) \quad \rho_N = |\Psi|^2 \quad \Psi$$

HF, CIS

CCSD, etc.

CCSDT, etc. CCSDTQ, etc.

full-CI

Baerends, Buijse, Cioslowski, Coleman, Davidson, Donnelly, Garrod, Goedecker, Levy, Mazziotti, Parr, Percus, Piris, Umrigar, Valdemoro...

Davidson, Furche, Higuchi, Higuchi, Levy, Nagy, Pistol, Samvelyan, Weinhold, Wilson, Ziesche, ...

"classic" quantum chemistry; Pople, Davidson, and Löwdin "schools"

"Polydensity" alternative: Gori-Giorgi, Percus, Savin.

The electronic Hamiltonian contains only one- and two-body operators.

$$\begin{aligned} E_{g.s.} [v; N] \\ = & \frac{N}{2} \iint \cdots \int \Psi^* (\mathbf{z}_1, \dots, \mathbf{z}_N) \left(-\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 \right) \Psi (\mathbf{z}_1, \dots, \mathbf{z}_N) d\mathbf{z}_1 \dots d\mathbf{z}_N \\ & + \frac{N}{2} \iint \cdots \int \Psi^* (\mathbf{z}_1, \dots, \mathbf{z}_N) \left(v(\mathbf{z}_1) + v(\mathbf{z}_2) \right) \Psi (\mathbf{z}_1, \dots, \mathbf{z}_N) d\mathbf{z}_1 \dots d\mathbf{z}_N \\ & + \frac{N(N-1)}{2} \iint \cdots \int \Psi^* (\mathbf{z}_1, \dots, \mathbf{z}_N) \left(\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \Psi (\mathbf{z}_1, \dots, \mathbf{z}_N) d\mathbf{z}_1 \dots d\mathbf{z}_N \end{aligned}$$

⇒ The full wavefunction is not required to evaluate the ground-state energy.

Because electrons are identical particles, if we really understood what just two electrons were doing, we could infer the energetic contributions of the remaining electrons.

The **kinetic energy** and **electron-electron repulsion** operators are “universal.”

$$\begin{aligned} E_{g.s.}[v; N] \\ = \frac{N}{2} \iint \cdots \int \Psi^*(\mathbf{z}_1, \dots, \mathbf{z}_N) \left(-\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 \right) \Psi^*(\mathbf{z}_1, \dots, \mathbf{z}_N) d\mathbf{z}_1 \dots d\mathbf{z}_N \\ + \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} \\ + \frac{N(N-1)}{2} \iint \cdots \int \Psi^*(\mathbf{z}_1, \dots, \mathbf{z}_N) \left(\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \Psi^*(\mathbf{z}_1, \dots, \mathbf{z}_N) d\mathbf{z}_1 \dots d\mathbf{z}_N \end{aligned}$$

⇒ The **electron density** can be used as the fundamental descriptor for electronic systems.

“Unknown” functionals: **kinetic energy**
electron-electron repulsion

P. Hohenberg and W. Kohn, Phys.Rev. **136**, B864 (1964); M. Levy, Proc. Natl. Acad. Sci. **76**, 6062 (1979); E. H. Lieb, Int. J. Quantum Chem. **24**, 243 (1983).

The **electron-electron repulsion** potential is “universal.”

$$\begin{aligned} E_{g.s.}[v; N] \\ = \iint \delta(\mathbf{z}_1 - \mathbf{z}'_1) \left(\left(\hat{t}(\mathbf{z}_1) + v(\mathbf{z}_1) \right) \gamma(\mathbf{z}_1, \mathbf{z}'_1) \right) d\mathbf{z}_1 d\mathbf{z}'_1 \\ + \frac{N(N-1)}{2} \iint \dots \int \Psi^*(\mathbf{z}_1, \dots, \mathbf{z}_N) \left(\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \Psi^*(\mathbf{z}_1, \dots, \mathbf{z}_N) d\mathbf{z}_1 \dots d\mathbf{z}_N \end{aligned}$$

⇒ The **one-electron reduced density matrix** suffices as the fundamental descriptor for electronic systems.

Unknown functionals: **electron-electron repulsion**

M. Levy, Proc. Natl. Acad. Sci. 76, 6062 (1979); R. A. Donnelly and R. G. Parr, J. Chem. Phys. 69, 4431 (1978).

The **kinetic energy** operator is “universal.”

$$\begin{aligned} E_{g.s.}[v; N] \\ = \frac{N}{2} \iint \cdots \int \Psi^*(\mathbf{z}_1, \dots, \mathbf{z}_N) \left(-\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 \right) \Psi^*(\mathbf{z}_1, \dots, \mathbf{z}_N) d\mathbf{z}_1 \dots d\mathbf{z}_N \\ + \iint \rho_2(\mathbf{z}_1, \mathbf{z}_2) \left(\frac{v(\mathbf{z}_1) + v(\mathbf{z}_2)}{2(N-1)} + V_{rep}(\mathbf{z}_1, \mathbf{z}_2) \right) d\mathbf{z}_1 d\mathbf{z}_2 \end{aligned}$$

⇒ The **electron pair density** can be used as the fundamental descriptor for electronic systems.

Unknown functionals: **kinetic energy**

“Unknown” N -representability problem.

P. Ziesche, Phys. Lett. A 195, 213 (1994).; M. Levy and P. Ziesche, J. Chem. Phys. 115, 9110 (2001); PWA J. Math. Phys. 46, 062107 (2005); PWA Phys. Rev. A 74, 042502 (2006).

The electronic Hamiltonian contains only one- and two-body operators.

$$E_{g.s.}[v; N]$$

$$= \iiint \delta(\mathbf{z}_1 - \mathbf{z}'_1) \delta(\mathbf{z}_2 - \mathbf{z}'_2) \left(\hat{h}_{v,N}(\mathbf{z}_1, \mathbf{z}_2) \Gamma_2(\mathbf{z}_1, \mathbf{z}_2; \mathbf{z}'_1, \mathbf{z}'_2) \right) d\mathbf{z}_1 d\mathbf{z}_2 d\mathbf{z}'_1 d\mathbf{z}'_2$$

$$\hat{h}_{v,N}(\mathbf{z}_1, \mathbf{z}_2) = \frac{2}{N-1} \left(\hat{t}(\mathbf{z}_1) + \hat{t}(\mathbf{z}_2) + v(\mathbf{z}_1) + v(\mathbf{z}_2) \right) + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

⇒ The **two-electron reduced density matrix** can be used as the fundamental descriptor for electronic systems.

Unknown functionals: **NONE!!**

“Unknown” *N*-representability problem.

PWA, S. Golden, M. Levy, J. Chem. Phys. 124, 054101 (2006)

PWA, M. Levy, J. Chem. Sci. 117, 507 (2005)

Spatial Representation:

$$E_{g.s.}[\nu; N]$$

$$= \iiint \delta(\mathbf{z}_1 - \mathbf{z}'_1) \delta(\mathbf{z}_2 - \mathbf{z}'_2) \left(\hat{h}_{v,N}(\mathbf{z}_1, \mathbf{z}_2) \Gamma_2(\mathbf{z}_1, \mathbf{z}_2; \mathbf{z}'_1, \mathbf{z}'_2) \right) d\mathbf{z}_1 d\mathbf{z}_2 d\mathbf{z}'_1 d\mathbf{z}'_2$$

Orbital representation:

$$E_{g.s.}[\nu; N] = \text{Tr}[\mathbf{h} \cdot \mathbf{\Gamma}]$$

$$\Gamma_2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2) = \sum_{iji'j'} \Gamma_{iji'j'} \phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_2) \phi_{i'}^*(\mathbf{r}'_1) \phi_{j'}^*(\mathbf{r}'_2)$$

$$\Gamma_{iji'j'} = \binom{N}{2} \sum_K w_K \iiint \left(\Psi_K^*(\mathbf{r}'_1, \mathbf{r}'_2, \mathbf{r}_3, \dots, \mathbf{r}_N) \phi_{i'}(\mathbf{r}'_1) \phi_{j'}(\mathbf{r}'_2) \right. \\ \left. \times \phi_i^*(\mathbf{r}_1) \phi_j^*(\mathbf{r}_2) \Psi_K(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \right) d\mathbf{r}_1 d\mathbf{r}'_1 \dots d\mathbf{r}_N$$

$$\Gamma_{iji'j'} = \sum_K w_K \left\langle \Psi_K \left| a_{i'}^+ a_{j'}^+ a_j a_i \right| \Psi_K \right\rangle$$

In applications of interests to chemists,
the number of $\{\phi_k\}$ is often ~ 200 .

For Be:

$$-18 E_h = \underbrace{\min}_{\left\{ \Gamma_2 \left| \begin{array}{l} \text{Tr}[\Gamma] = \binom{N}{2} \\ \Gamma \succeq 0 \end{array} \right. \right\}} \text{Tr}[\mathbf{h} \cdot \Gamma]$$

This is very bad but that's expected; the analogous 1-RDM calculation:

$$\underbrace{\min}_{\left\{ \gamma \left| \begin{array}{l} \text{Tr}[\gamma] = N \\ \gamma \succeq 0 \end{array} \right. \right\}} \text{Tr}[(\hat{t} + v) \cdot \gamma] + V_{ee}[\gamma]$$

is *very bad* (even worse).

A good 1-RDM calculation must constrain the holes also

$$E_{g.s.} \equiv \underbrace{\min}_{\left\{ \gamma \left| \begin{array}{l} \text{Tr}[\gamma] = N \\ \gamma \succeq 0 \\ \mathbf{I} - \gamma \succeq 0 \end{array} \right. \right\}} \text{Tr} \left[(\hat{t} + v) \cdot \gamma \right] + V_{ee} [\gamma]$$

A “fair comparison” is

$$-14.61 E_h = \underbrace{\min}_{\left\{ \Gamma_2 \left| \begin{array}{l} \text{Tr}[\Gamma] = \binom{N}{2} \\ \Gamma \succeq 0; \mathbf{Q}(\Gamma) \succeq 0 \end{array} \right. \right\}} \text{Tr} [\mathbf{h} \cdot \Gamma]$$

$$\mathbf{Q}(\Gamma) = \sum_K w_K \left\langle \Psi_K \left| a_i a_j a_{j'}^+ a_{i'}^+ \right| \Psi_K \right\rangle \succeq 0$$

This is ca. 20 milliHartree below the full-CI energy in this basis.

J. Coleman, Reviews of Modern Physics **35**, 668 (1963).

The problem is that the density matrix has to correspond to *some* N -fermion system.

Γ_2 is **N-representable** if and only if there exists some N -fermion system with:

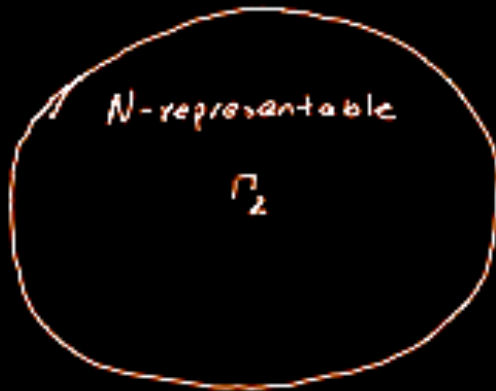
$$\Gamma_{ijij'} = \sum_K w_K \left\langle \Psi_K(\mathbf{z}_1 \dots \mathbf{z}_N) \left| a_{i'}^+ a_{j'}^+ a_j a_i \right| \Psi_K(\mathbf{z}_1 \dots \mathbf{z}_N) \right\rangle$$

$$0 \leq w_K \leq 1;$$

$$1 = \sum_K w_K$$

The exact ground-state energy is obtained from:

$$E_{g.s.} \equiv \underbrace{\min}_{\left\{ \Gamma_2 \left| \begin{array}{l} \text{Tr}[\Gamma] = \binom{N}{2} \\ \Gamma \text{ is } N\text{-representable} \end{array} \right. \right\}} \text{Tr}[\mathbf{h} \cdot \Gamma]$$



The set of N -representable Γ_2 is **closed** and **convex**.

$$\Gamma_{ij'i'j'} = \sum_K w_K \left\langle \Psi_K(\mathbf{z}_1 \dots \mathbf{z}_N) \left| a_{i'}^+ a_{j'}^+ a_j a_i \right| \Psi_K(\mathbf{z}_1 \dots \mathbf{z}_N) \right\rangle$$

$$0 \leq w_K \leq 1;$$

$$1 = \sum_K w_K$$

The exact N -representability conditions are known, but not in a useful form.

Suppose we had a non- N -representable Γ_2

N -representable
 Γ_2

• $\hat{\Gamma}_2$ ← not N -representable

Then there exists an element of the Hilbert Space that separates this defective density matrix, so that

$$\begin{aligned} \text{Tr}[\mathbf{H}\Gamma_{N\text{-rep}}] &\geq \underbrace{\min}_{\left\{ \Gamma \left| \begin{array}{l} \text{Tr}[\Gamma] = \binom{N}{2} \\ \Gamma \text{ is } N\text{-representable} \end{array} \right. \right\}} \text{Tr}[\mathbf{H}\Gamma] \\ &= E_{g.s.}[\mathbf{H}] > \text{Tr}[\mathbf{H}\tilde{\Gamma}_2] \end{aligned}$$

N -representable
 Γ_2

$$\text{Tr}[\mathbf{H}\Gamma_2] = E_{g.s.}[\mathbf{H}]$$

not N -representable

• $\tilde{\Gamma}_2$

N -representable
 Γ_2

$$\text{Tr}[\mathbf{H}\Gamma_2] = E_{g.s.}[\mathbf{H}]$$

not N -representable

• $\hat{\Gamma}_2$

For every Hamiltonian

$$\text{Tr}[\mathbf{H}\Gamma] \geq E_{g.s.}[\mathbf{H}]$$



Γ_2 is N -representable

Necessary and Sufficient Condition for N -rep.:

For **every Hamiltonian**

$$\text{Tr}[\mathbf{H}\Gamma] \geq E_{g.s.}[\mathbf{H}]$$



Γ_2 is N -representable

Restatement as a Semidefinite Problem:

For **every**

**positive-semidefinite
Hamiltonian**



Γ_2 is N -representable

$$\text{Tr}\left[\left(\mathbf{H} - \mathbf{I} \cdot E_{g.s.}(\mathbf{H})\right)\Gamma\right] \geq 0$$

Approximation as a Semidefinite Problem:

For **some class of**

**positive-semidefinite
Hamiltonians**



Γ_2 is N -representable

$$\text{Tr}\left[\left(\mathbf{H} - \mathbf{I} \cdot E_{g.s.}(\mathbf{H})\right)\Gamma\right] \geq 0$$

C. Garrod and J. K. Percus, J. Math. Phys. 5, 1756 (1964).

Standard Approximate N-representability Conditions

Manifestly positive-definite Hamiltonians:

$$\mathbf{B}^+ \mathbf{B} \succeq 0$$

where

$$\text{P:} \quad \mathbf{B} = p_{ij} a_j a_i \quad p_{ij} = -p_{ji}$$

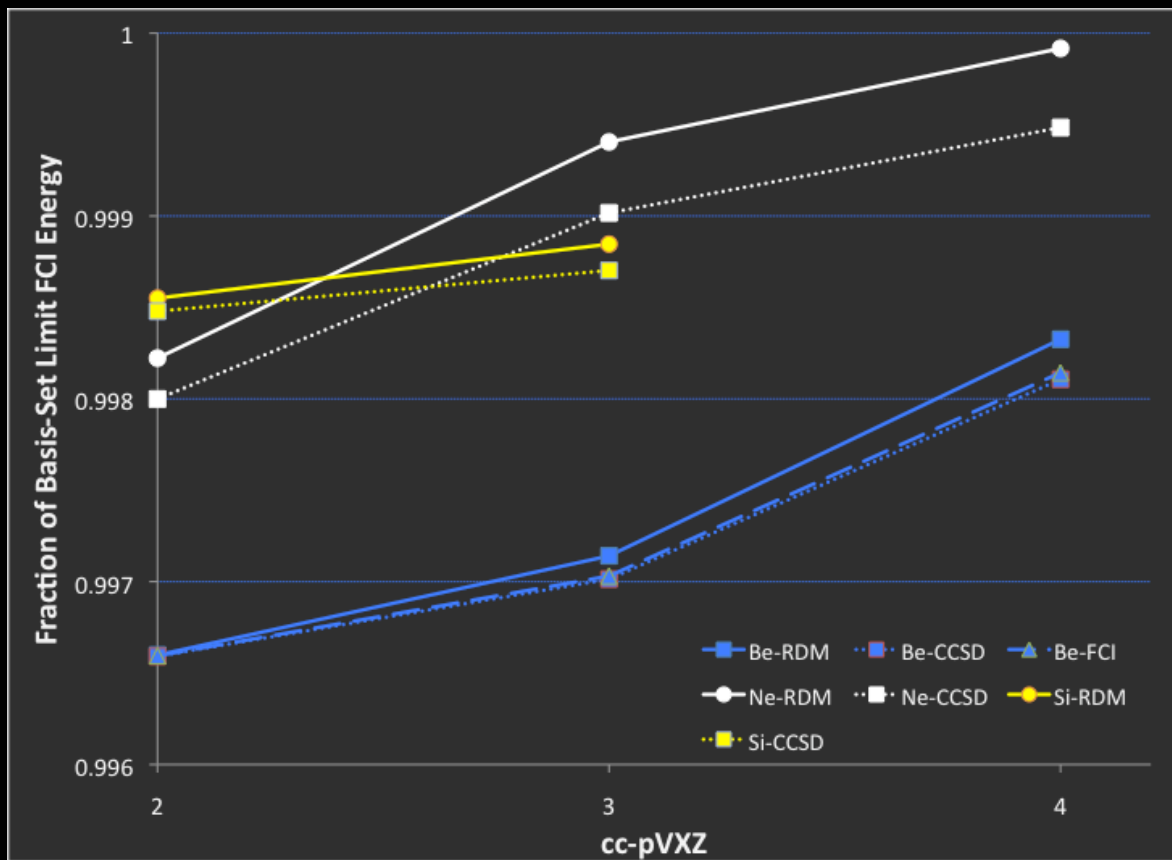
$$\text{Q:} \quad \mathbf{B} = q_{ij} a_j^+ a_i^+ \quad q_{ij} = -q_{ji}$$

$$\text{G:} \quad \mathbf{B} = g_{ij} a_j^+ a_i$$

For Be (cc-pVQZ; Full-CI -14.6401 E_h):

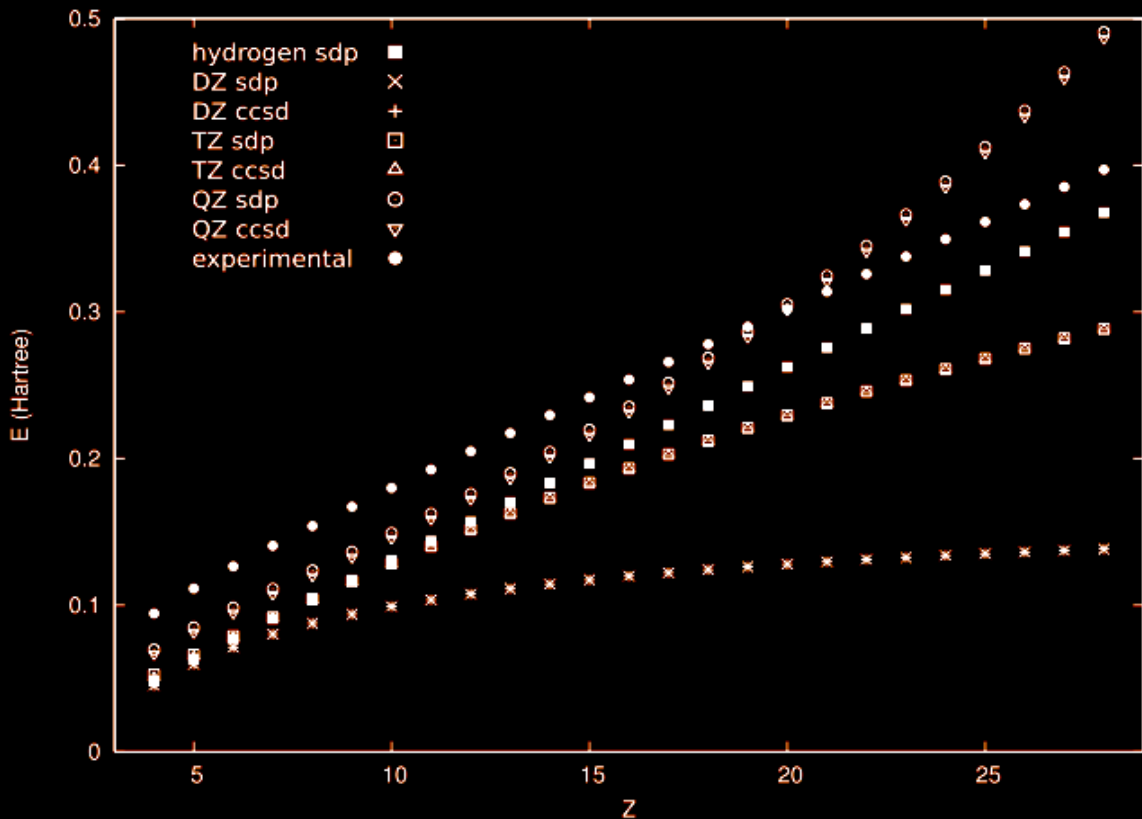
$$-14.6428 E_h = \min_{\left\{ \Gamma_2 \left| \begin{array}{l} \text{Tr}[\Gamma] = \binom{N}{2} \\ \text{G}(\Gamma) \succeq 0 \end{array} \right. \right\}} \text{Tr}[\mathbf{h} \cdot \Gamma]$$

Part of the game is to find better N -representability conditions....but the above constraints are often “adequate.”

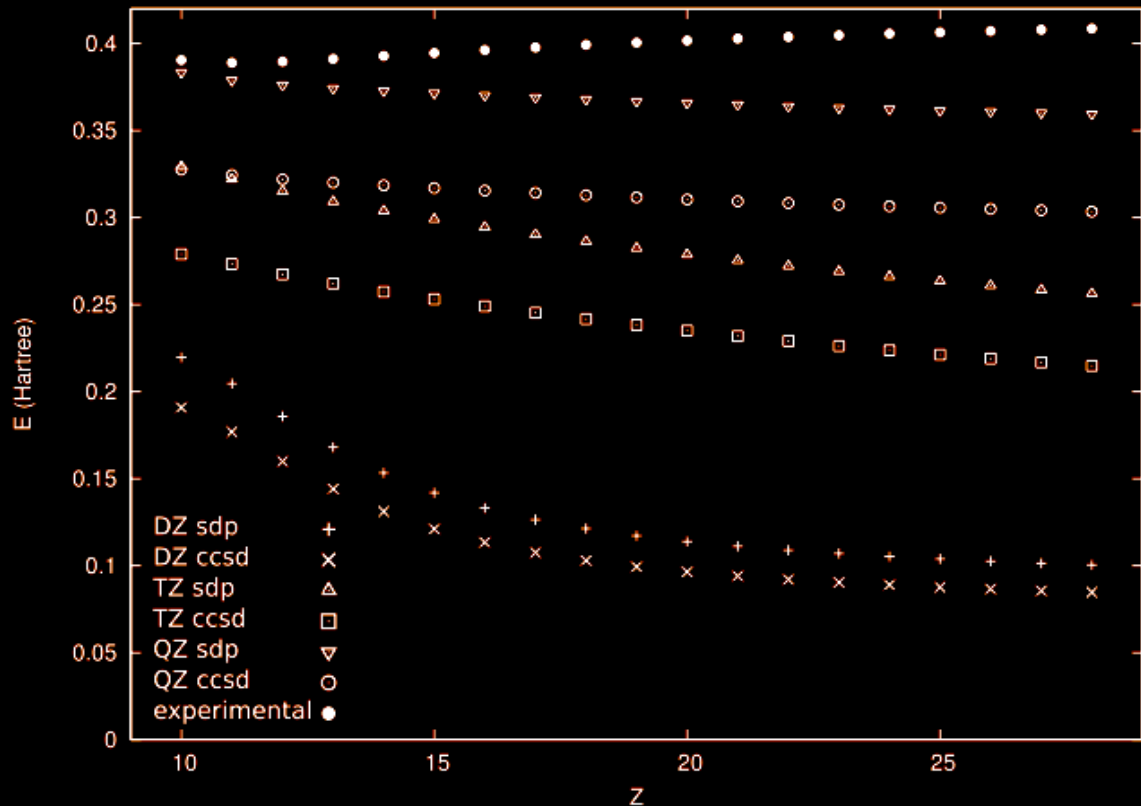


Basis-set Stability is OK....

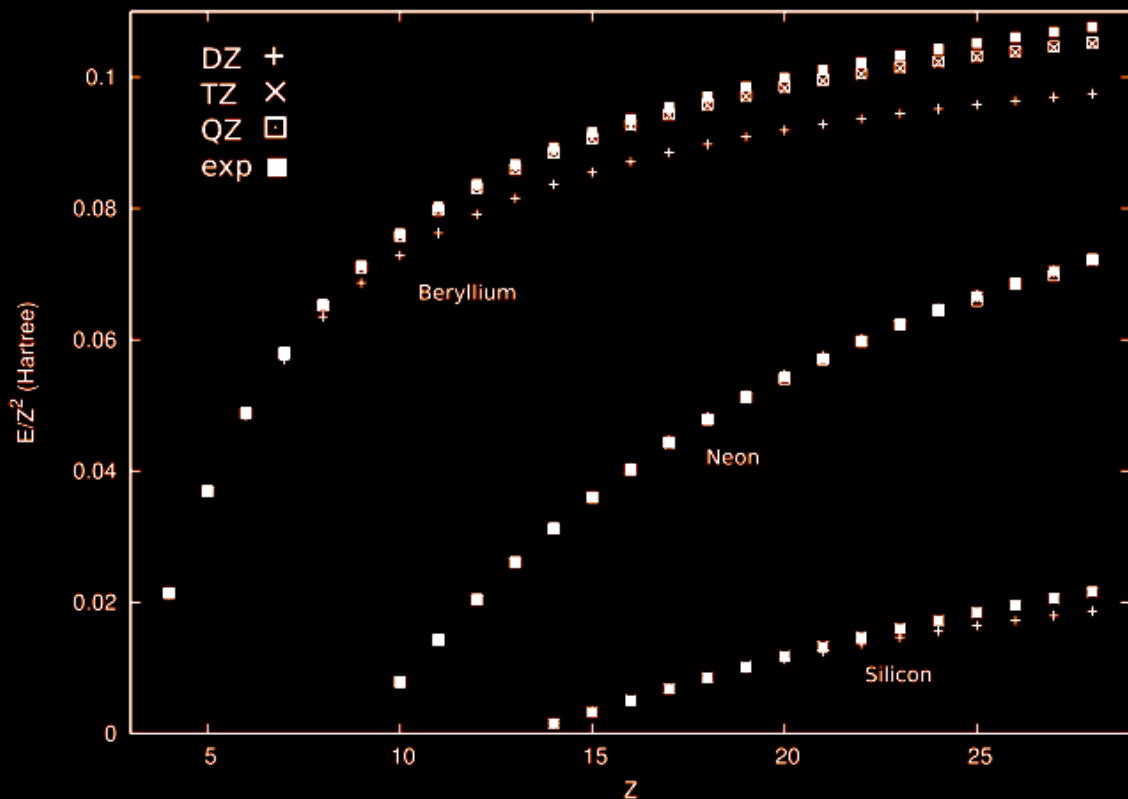
Correlation Energy vs. Atomic Number for Be Isoelectronic Series



Correlation Energy vs. Atomic Number for Ne Isoelectronic Series

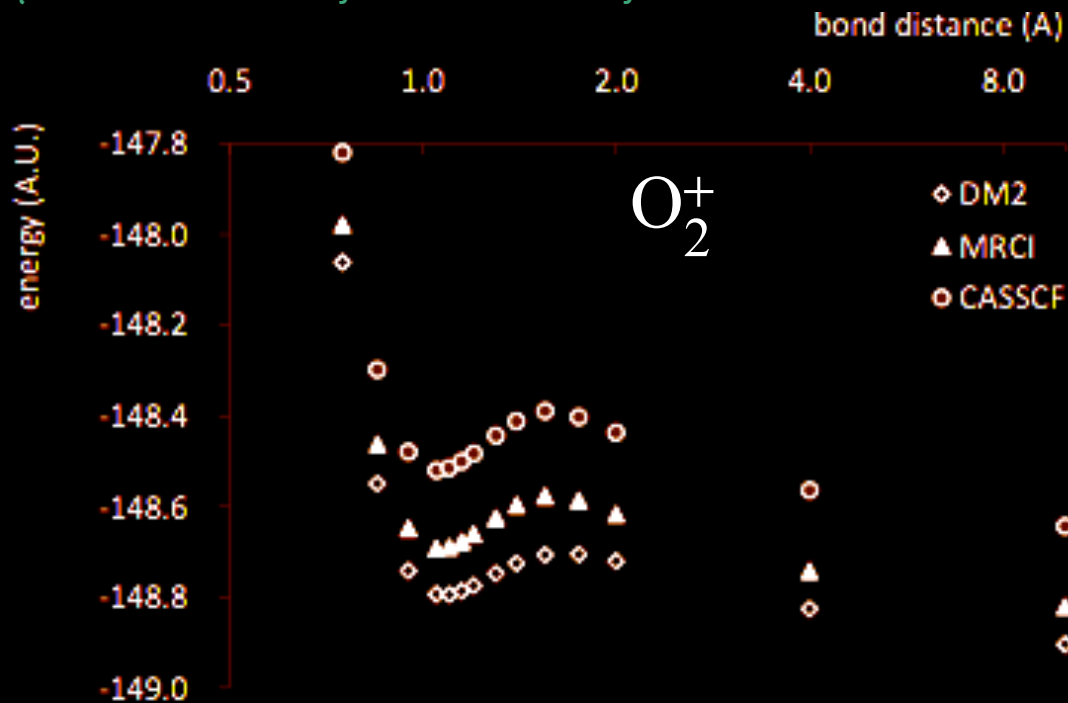


Ionization Potentials from Extended Koopmans' Theorem

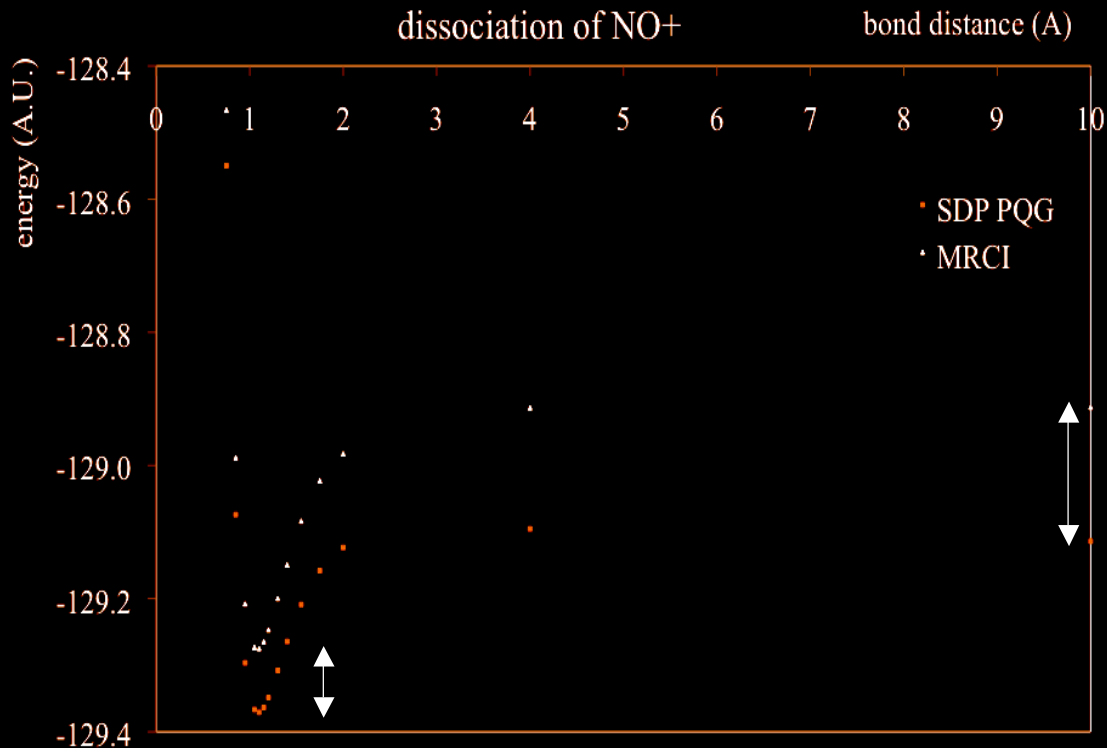


What about Molecules?

P+Q+G does well in cases where some conventional quantum chemistry methods badly fail.



But...Dissociation is *qualitatively* wrong for NO^+ .



Population Analysis N = 6.53 electrons; O = 7.47 electrons.

Adding the 3-index T1 and T2 constraints does not help.

This Happens for All Heteronuclear Diatomics

(except those containing Group 1 and Group 2 elements, H, He, Li, Be, Na, Mg, etc.)

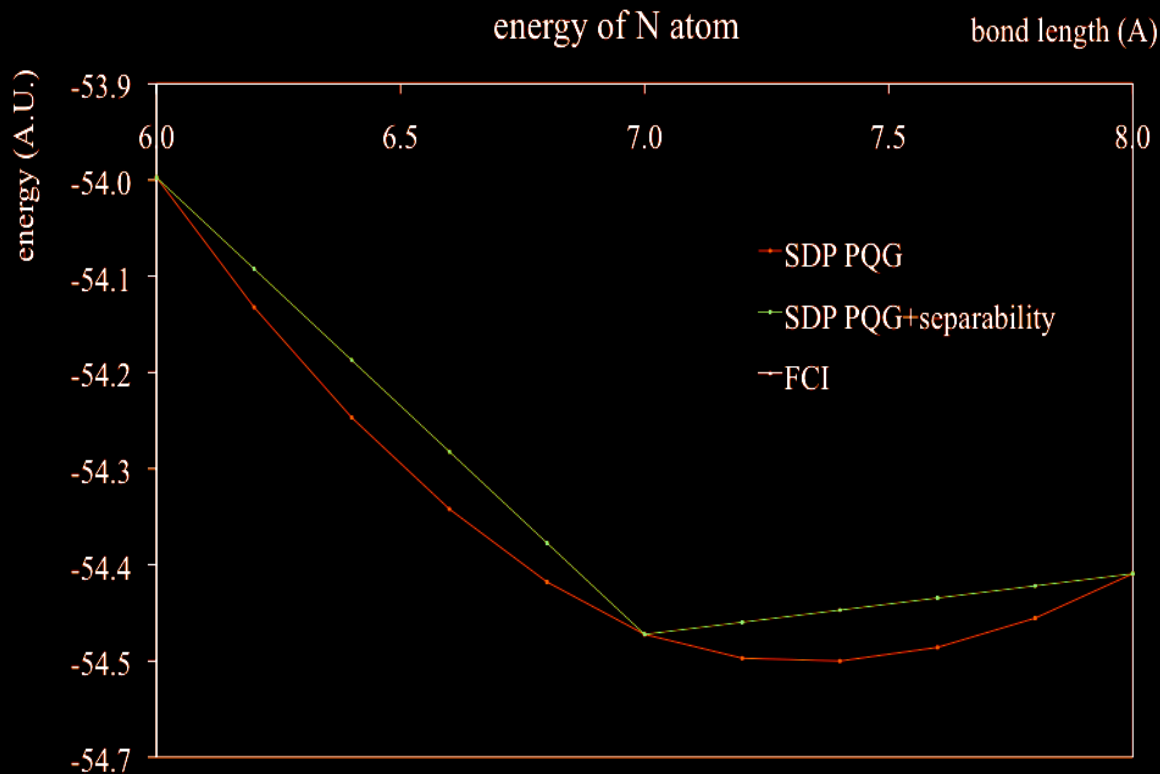
Dipole Moments for Heteronuclear Diatomics

	MRCI (10 Å)	DM2 (10 Å)	DM2 (20Å)
NO^+	22.40	-0.11	-0.29
CN^-	25.83	7.01	13.38
CO	0.00	-0.90	-1.71

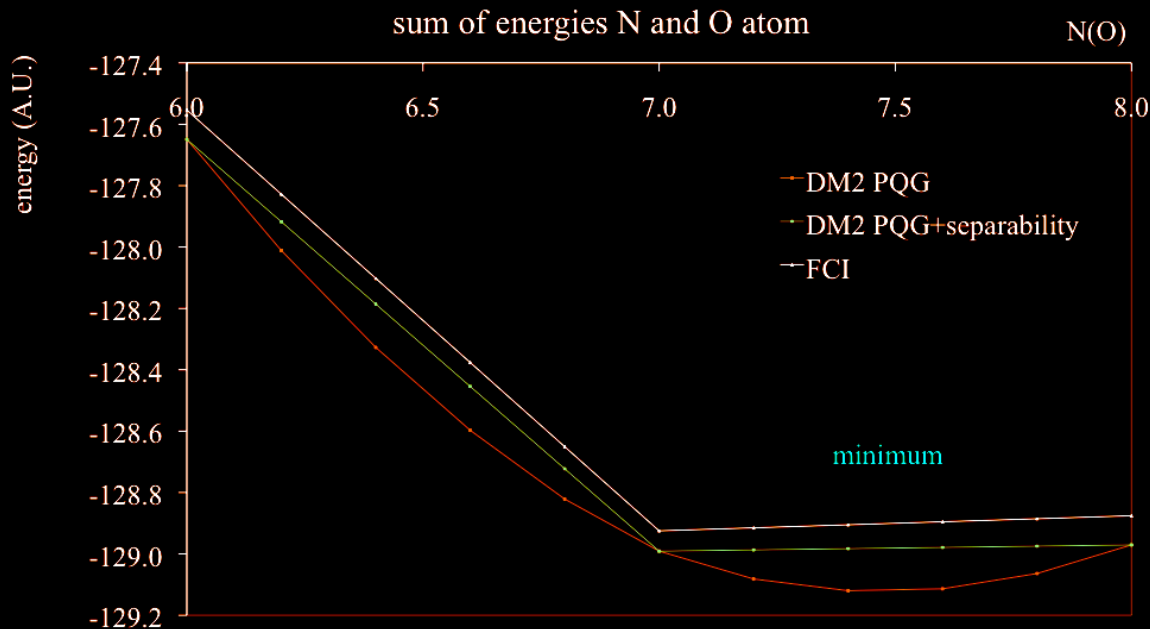
Dissociation Energies and Population Analysis

Reaction	MPA	ΔE_1
$\text{N}_2 \rightarrow \text{N} + \text{N}$	7.00/7.00	-0.0035
$\text{CO} \rightarrow \text{C} + \text{O}$	5.98/8.02	-0.0036
$\text{NO}^+ \rightarrow \text{N} + \text{O}^+$	6.53/7.47	-0.1291
$\text{CN}^- \rightarrow \text{C}^- + \text{N}$	6.60/7.40	-0.0734

The problem is the lack of a derivative discontinuity:



Add together the Energy vs. N curves for N and O:



E vs. N Minimum: $N = 6.51$ electrons; $O = 7.49$ electrons.

RDM Population Analysis: $N = 6.53$ electrons; $O = 7.47$ electrons.

Energy difference between the RDM calculation and the E vs. N model: $.002 E_h$.

What is the correct behavior of $E(\Gamma_2)$ for non-integer N ?

Consider two identical N_0 -electron systems, infinitely far apart

$$A_1 \underbrace{\cdots \cdots \cdots}_{R \rightarrow \infty} A_2$$

Add one electron to the system. Consider the totally symmetric ground-state wavefunction:

$$\Psi_{A_1 \cdots A_2} = \frac{1}{2} \left(\Psi_{N_0+1}^{(A_1)} \wedge \Psi_{N_0}^{(A_2)} + \Psi_{N_0}^{(A_1)} \wedge \Psi_{N_0+1}^{(A_2)} \right)$$

$$E_{A_1 \cdots A_2} = \frac{1}{2} \left(E_{N_0}^{(A)} + E_{N_0+1}^{(A)} \right)$$

Because the subsystems are infinitely far apart, they are distinguishable. Because they are identical, we can identify the energy of a single subsystem as:

$$E_{N_0+\frac{1}{2}}^{(A)} = \frac{1}{2} E_{N_0}^{(A)} + \frac{1}{2} E_{N_0+1}^{(A)}.$$

Caveat: only true if E vs. N is convex. This is unproved and it is untrue (by counterexample) for r - k interparticle repulsions with $k > \log_3 4 \approx 1.3$.

Generalization of this argument to K copies of the system and $0 < J < K$ extra electrons:



$$\Psi = \binom{K}{J}^{-1/2} \sum_{\substack{\kappa_1 + \kappa_2 + \dots + \kappa_K = J \\ \kappa_1, \kappa_2, \dots, \kappa_K \in \{0, 1\}}} \left(\Psi_{N_0 + \kappa_1}^{(A_1)} \wedge \dots \wedge \Psi_{N_0 + \kappa_K}^{(A_K)} \right)$$

$$E_{A_1} = \dots = E_{A_K} = \left(1 - \frac{J}{K} \right) E_{N_0}^{(A)} + \frac{J}{K} E_{N_0+1}^{(A)}$$

J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz, Jr., Phys. Rev. Lett. 49, 1691 (1982); W. T. Yang, Y. K. Zhang, and PWA, Phys. Rev. Lett. 84, 5172 (2000); PWA, J. Math. Chem. 43, 285 (2008).

Qualitatively incorrect results are obtained when the derivative discontinuity is not reproduced. Some big problems:

- Incorrect dissociation products. (Fractional charges at infinite separation.)
- Incorrect spectroscopic constants. (Dissociation energy is too small.)
- Incorrect atomization energies for molecules.
- **Polarizability is too large.**
- **Reaction barriers in chemical reactions are far too small, and often nonexistent.**
- **Reaction rates are off by orders of magnitude.**
- **Charge-transfer energies are qualitatively incorrect.**

A Quantum Subsystem Constraint

Define the density matrices of a subsystem by:

$$\Gamma_{ab;a'b'}^{(\text{sub})} = \begin{cases} \Gamma_{ab;a'b'} & a, b, a'b' \in \mathcal{S} \\ 0 & \text{otherwise} \end{cases}$$
$$\gamma_{aa'}^{(\text{sub})} = \begin{cases} \sum_j \Gamma_{aj;a'j} & a, a' \in \mathcal{S} \\ 0 & \text{otherwise} \end{cases}$$

Then

$$\text{Tr} \left[\hat{h}_1^{(\text{sub})} \gamma^{(\text{sub})} \right] + \text{Tr} \left[V^{(\text{sub})} \Gamma^{(\text{sub})} \right] \geq E_{\text{Tr} \left[\gamma^{(\text{sub})} \right]}$$

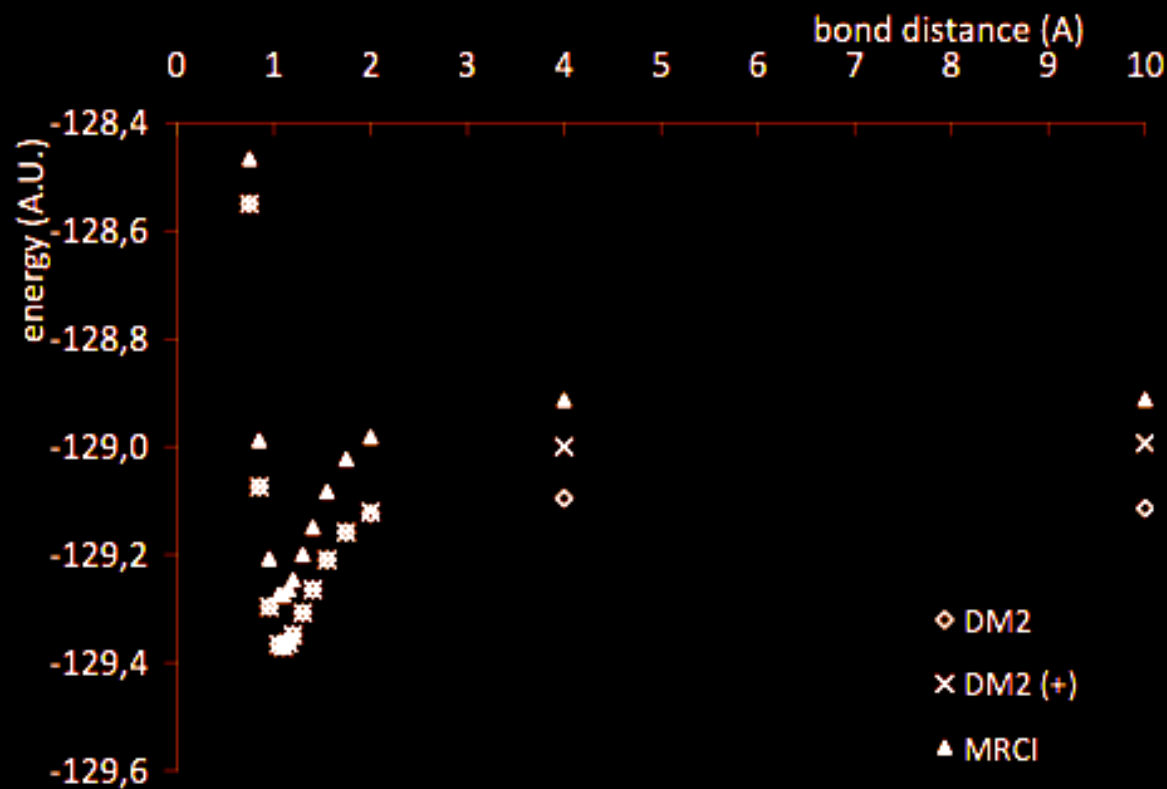
The energy on the right-hand-side of this equation is the correct “fractional N ” energy.

This must be true for *any* Hamiltonian and, in particular, for the atomic Hamiltonians.

1. Choose the Hamiltonians to the Hamiltonians of the atoms.
2. Choose the subsystems to be the basis functions centered on the atoms.
3. Obtain a lower bound on the fractional N energy by solving the density-matrix problem for the subsystem Hamiltonian.
4. Solve the molecular problem with the additional constraints of the form

$$\text{Tr} \left[\hat{h}_1^{(\text{sub})} \gamma^{(\text{sub})} \right] + \text{Tr} \left[V^{(\text{sub})} \Gamma^{(\text{sub})} \right] \geq E_{\text{Tr} \left[\gamma^{(\text{sub})} \right]}$$

This additional constraint forces the dissociation limit to be correct. It also imposes size-consistency: the energy of a sum of disjoint, separated, subsystems must be equal to the sum of the energies of the individual components of the system.



	R (Å)	DM2	DM2 (+)	MRCI
NO ⁺	4.0	-129.0952	-129.0002	-128.9133
	10.0	-129.1138	-128.9928	-128.9125
	20.0	-129.1202	-128.9917	
CN ⁻	4.0	-92.3634	-92.3237	-92.2387
	10.0	-92.3790	-92.3130	-92.2365
	20.0	-92.3851	-92.3123	
CO	4.0	-112.7744	-112.7730	-112.6657
	10.0	-112.7726	-112.7702	-112.6651
	20.0	-112.7725	-112.7697	
N ₂	4.0	-109.0344	-109.0336	-108.9520
	10.0	-109.0333	-109.0309	-108.9518
	20.0	-109.0332	-109.0302	
O ₂ ²⁺	4.0	-148.8261	-148.8250	-148.7415
	10.0	-148.9043	-148.9011	-148.8200
	20.0	-148.9305	-148.9267	

Dipole Moments are OK now

	R (Å)	DM2	DM2 (+)	MRCI
NO ⁺	4.0	0.07	5.74	8.76
	10.0	-0.11	20.97	22.39
	20.0	-0.29	44.23	
CN ⁻	4.0	3.35	8.34	9.94
	10.0	7.01	25.77	25.83
	20.0	13.38	52.11	
CO	4.0	-0.40	-0.04	0.04
	10.0	-0.90	0.00	0.00
	20.0	-1.71	0.00	

“Popular” Algorithms for 2-RDM Optimization

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- M. Nakata, H. Nakatsuji, M. Ehara, M. Fukuda, K. Nakata, and K. Fujisawa, J. Chem. Phys. **114**, 8282 (2001).
- D. A. Mazziotti, Phys. Rev. Lett. **93**, 213001 (2004).
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In order to be competitive, a P+Q+G calculation must:

- scale as k^6 with respect to the one-electron basis. I.e., the scaling should be $\sim \dim(\Gamma_2)^3$.
- have a computational prefactor small enough for calculations with $k \sim 200$ to be practical. ($\dim(\Gamma_2) \sim 10^4$)

$$E_{g.s.} \left[v; N \right] = \lim_{t \rightarrow 0^+} \underbrace{\min}_{\Gamma} f_t(\Gamma)$$

$$f_t(\Gamma) = \text{Tr} \left[\mathbf{h}_{v,N} \Gamma \right] - t \left(\ln |\Gamma| + \ln |\mathbf{Q}(\Gamma)| + \ln |\mathbf{G}(\Gamma)| + \dots \right)$$

We regard the \mathbf{Q} and \mathbf{G} conditions as linear and Hermitian mappings of Γ_2 .

We express Γ_2 in a geminal basis and define the “unit basis” for the matrices as:

$$\Gamma = \sum_{IJ} \Gamma_{IJ} \mathbf{F}^{(IJ)}$$

$$\mathbf{F}^{(IJ)} = \left[f_{ij} = \delta_{ij, IJ} \right]$$

$$E_{g.s.}[\nu; N] = \varliminf_{t \rightarrow 0^+} f_t(\Gamma)$$

$$f_t(\Gamma) = \text{Tr}[\mathbf{h}_{\nu, N} \Gamma] - t \left(\ln |\Gamma| + \ln |\mathbf{Q}(\Gamma)| + \ln |\mathbf{G}(\Gamma)| + \dots \right)$$

The gradient and the action of the Hessian on a vector are easy to construct. E.g.,

$$\begin{aligned} \nabla f_t(\Gamma) &\equiv \frac{\partial f_t(\Gamma)}{\partial \Gamma_{IJ}} = \mathbf{h}_{\nu, N} - t \left(\begin{aligned} &\text{Tr}[\Gamma^{-1} \mathbf{F}^{(IJ)}] + \text{Tr}[[\mathbf{Q}(\Gamma)]^{-1} \mathbf{Q}(\mathbf{F}^{(IJ)})] \\ &+ \text{Tr}[[\mathbf{G}(\Gamma)]^{-1} \mathbf{G}(\mathbf{F}^{(IJ)})] + \dots \end{aligned} \right) \\ &= \mathbf{h}_{\nu, N} - t \left(\begin{aligned} &\text{Tr}[\Gamma^{-1} \mathbf{F}^{(IJ)}] + \text{Tr}[\mathbf{Q}([\mathbf{Q}(\Gamma)]^{-1}) \mathbf{F}^{(IJ)}] \\ &+ \text{Tr}[\mathbf{G}([\mathbf{G}(\Gamma)]^{-1}) \mathbf{F}^{(IJ)}] + \dots \end{aligned} \right) \end{aligned}$$

$$E_{g.s.} [v; N] = \lim_{t \rightarrow 0^+} \underbrace{\min}_{\Gamma} f_t(\Gamma)$$

$$f_t(\Gamma) = \text{Tr}[\mathbf{h}_{v,N} \Gamma] - t \left(\ln |\Gamma| + \ln |\mathbf{Q}(\Gamma)| + \ln |\mathbf{G}(\Gamma)| + \dots \right)$$

1. **Guess the density matrix with penalty strength t .**
2. **Compute Newton Step Direction (“truncated Newton”)**

$$\nabla \nabla f_t(\Gamma) \cdot (\Delta \Gamma) = -\nabla f_t(\Gamma)$$
3. **Perform line search in Newton direction.**
4. **If not converged, go back to step 2. If converged, reduce t and go back to step 1.**

$$E_{g.s.}[\nu; N] = \varliminf_{t \rightarrow 0^+} f_t(\Gamma)$$

$$f_t(\Gamma) = \text{Tr}[\mathbf{h}_{\nu, N} \Gamma] - t \left(\ln |\Gamma| + \ln |\mathbf{Q}(\Gamma)| + \ln |\mathbf{G}(\Gamma)| + \dots \right)$$

1. Guess the density matrix with penalty strength t .

We extrapolate from solutions from previous values of t .

2. Compute Newton Step Direction (“truncated Newton”)

$$\nabla \nabla f_t(\Gamma) \cdot (\Delta \Gamma) = -\nabla f_t(\Gamma)$$

Precondition the linear equations. Use conjugate gradient or MINRES.
(Limited Memory) Quasi-Newton doesn't work.

3. Perform line search in Newton direction.

Very fast; equivalent to two gradient evaluations.

4. If not converged, go back to step 2. If converged, reduce t and go back to step 1.

In practice, very few Newton steps needed to converge.

Good News

- Exact N -representability conditions for Γ_2 are known.
- There is a systematic way to derive the full set of N -representability conditions.

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- There is a systematic way to derive the full set of N -representability conditions.

Bad News

- If exact N -representability conditions are not imposed, there always exists a system with an arbitrarily large error. (But that system may not be electronic.)

Good News

- **Basis Set Stability** seems OK.

Good News

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Bad News

- We still haven't used a large enough basis set to get the promised "lower bound" on the exact energy.

Good News

- $P+Q+G$ gives good results for atomic energies.
- $P+Q+G$ gives good results for single-electron properties of atoms like ionization potentials.
- An Dyson-orbital-like spectrum (and an “exact” first IP) can be obtained by extended Koopmans’ Theorem.

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- $P+Q+G$ gives good results for single-electron properties of atoms like ionization potentials.
- An Dyson-orbital-like spectrum (and an “exact” first IP) can be obtained by extended Koopmans’ Theorem.
- $P+Q+G (+T1+T2)$ gives a good description of molecules near equilibrium.

Bad News

- Dissociation of Heteronuclear Diatomic Molecules is Qualitatively Incorrect.

Good News

- The subspace-representability constraint fixes the dissociation problem for heteronuclear diatomics and also improves the “near equilibrium” region of the curve.

Good News

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Bad News

- The cost of the subspace-representability constraint grows exponentially ($\sim N_{\text{atoms}}!$) with the size of the system.

Good News

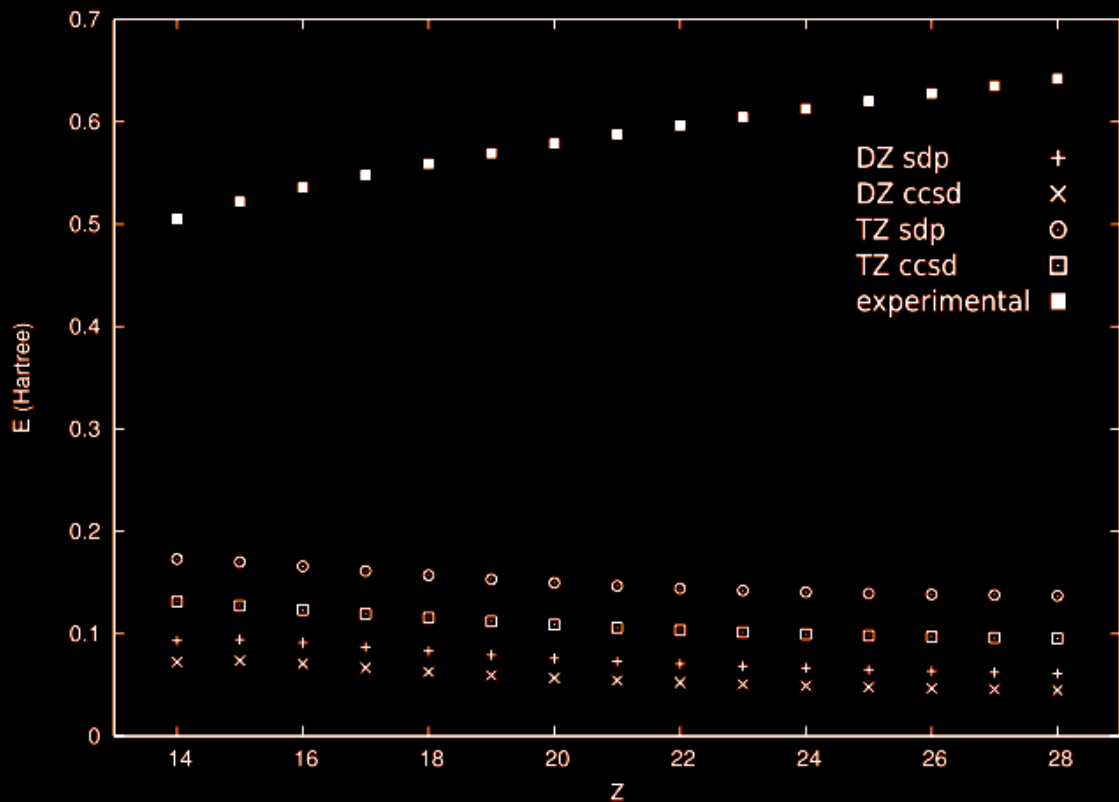
- 2-RDM calculations can be performed with N^6 scaling.

Good News

- 2-RDM calculations can be performed with N^6 scaling.

Bad News

- The prefactor is huge and current algorithms (at least our algorithm) is not competitive with the quantum chemistry competition (CCSD, etc.).



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