



Is there a 'Consistent' KS-DFT?

ES12

June 7, 2012

RODNEY J. BARTLETT

*Quantum Theory Project,
University of Florida, Gainesville, Florida USA*

Co-Workers

Prakash Verma, Ajith Perera, Matt Strasberg

Unconventional Use of CC Theory?

KOOPMANS' THM!

\$ AFOSR \$

CORRECT WAVEFUNCTION HAS TO BE AN EXPONENTIAL OF CONNECTED OPERATORS!

$$\Psi = \exp(T) |0\rangle$$

Hence, coupled-cluster theory!!!

- **SIZE-EXTENSIVE (No unlinked diagrams).**
- **RAPID SATURATION OF DYNAMIC CORRELATION**
- **CONNECTED EXPRESSIONS FOR AMPLITUDES (No CI evaluation.)**
- **INFINITE SUMMATION OF MBPT DIAGRAM**
 - **ITERATIONS GIVE MBPT(2), (3), (4), ...**
- **ANY PROPERTY, DENSITY MATRICES, ANALYTICAL GRADIENTS,
ANY SPECTRA, IR, RAMAN, NMR,...**
- **NO DECISIONS FOR USER EXCEPT BASIS, LEVEL OF CORRELATION**

R. J. Bartlett and M. Musial, "Coupled-cluster theory in quantum chemistry",
Revs. of Mod. Phys. **79**, 291-352 (2007).

EOM-CC FOR EXCITED STATES

$$(E_0 - H)\Psi_0 = 0 \quad \text{GROUND STATE}$$

$$(E_0 - H)\Psi_K = \omega_K \Psi_K \quad \text{EXCITED STATE}$$

$\Psi_K = R_k \exp(T)|0\rangle$ R_k is an operator that can create excited, ionized, or electron attached, doubly ionized,... states---

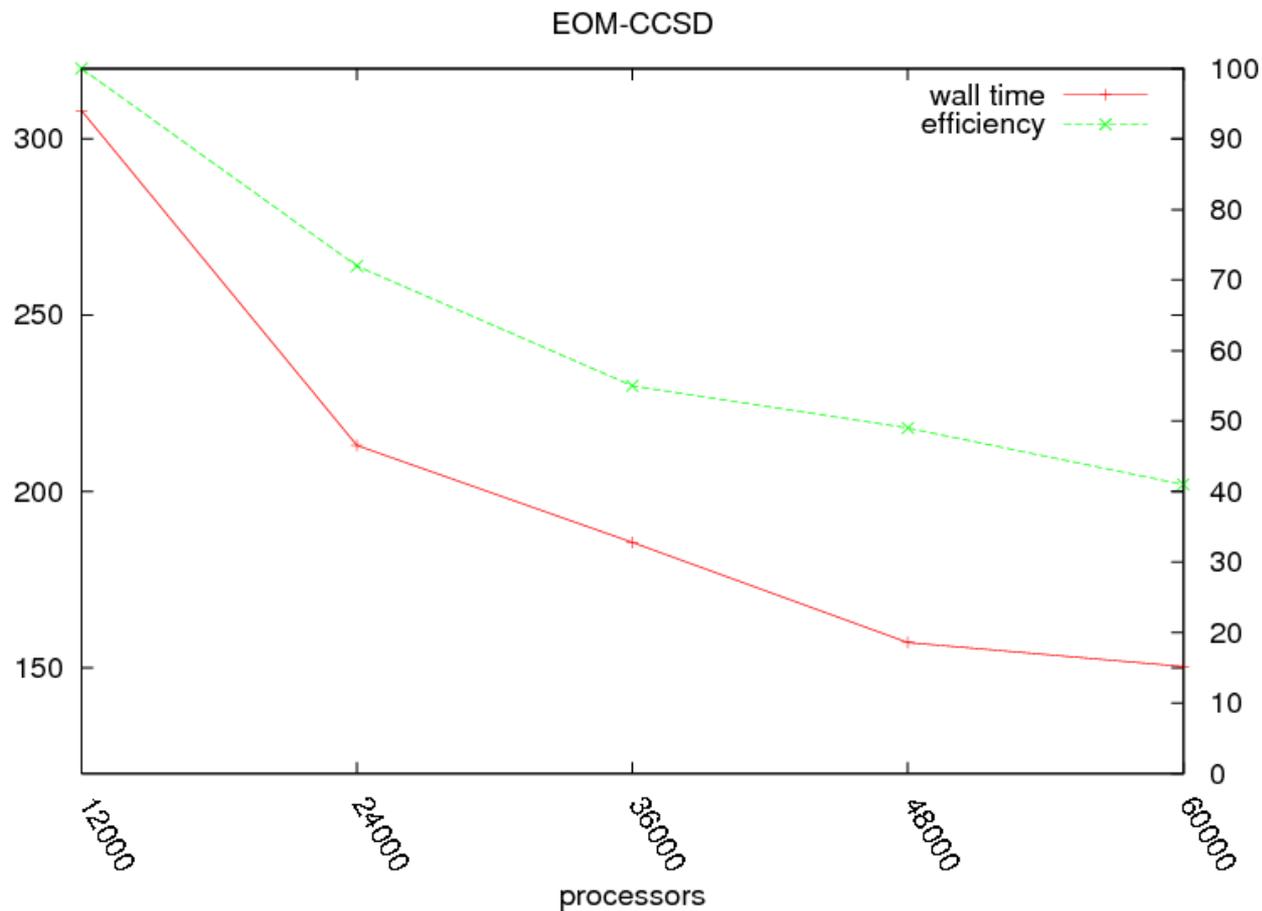
$$[T, R_k] = 0$$

Subtract the ground state equation from the excited state, to give

$$[e^{-T} H e^T, R_k]|0\rangle = (\mathbb{H}, R_k)_C |0\rangle = \omega_K R_k |0\rangle$$

$$\langle 0 | (L_k \mathbb{H}) = \langle 0 | L_k \omega_K$$

Example of a CC accessible problem: Cytosine-Guanine Watson-Crick stacked dimer



1154 basis functions
58 atoms
216 electrons

The alternative to explicit two-particle theories like CC, MBPT, CI, MCSCF, VB,...are effective independent particle theories---

$$h^{\text{eff}}(1)\varphi_p(1) = \varepsilon_p \varphi_p(1)$$

$$\Phi_0 = A(\varphi_1(1) \varphi_2(2) \dots \varphi_n(n))$$

$$h^{\text{eff}}(1) = t(1) + v(1) + J(1) + V_x(1) + V_c(1)$$

where all essential electron-correlation effects are hidden into an effective one-particle operator. DFT *formally* accomplishes this, along with some other options.

Critical to aufbau principles and photo-electron spectra is that $\varepsilon_k \approx -I(k)$.

Kohn-Sham Density Functional Theory (DFT)?

It's fast, cheap, 'correlated,' insensitive to most basis set extensions and easy to use. There is also the idea that further parameterizations will enable it to improve its predictions as in all semi-empirical theory.

But DFT is fatally flawed.

- (1) It cannot account for self-interaction (SIE). (Evaluate $\sum \langle ii | ii \rangle$ and see how big an error DFT introduces in step one. That has to be overcome subsequently in Exc[ρ],)
- (2) Its SIE affects activation barriers, ionization potentials, electron affinities, and Rydberg excited states.
- (3) It suffers from the integer-discontinuity condition.
- (4) It eliminates spin eigenstates and spin properties.
(How does it account for degeneracies in transition metal systems, as in multiplets?)
- (5) It cannot describe weak (vdW) interactions.
- (6) It does not account for charge-transfer in excited states.
- (7) But most of all, DFT does not guarantee convergence to the RIGHT answer!

Facts of Life

- All methods are special cases of the Schrödinger (Dirac) Eqn.
- Its coupled-cluster solutions, $\psi = (\exp(T) | \Phi \rangle$, and EOM-CC extensions, $\psi_X = R_X | \psi_0 \rangle$, $\omega_X = E_X - E_0$, provides the best **numerical solutions** available for the largest number of (CC accessible) problems.
- There are no self-interaction, dispersion, integer discontinuity, charge-transfer, long-range behavior,, problems.
- *(There are basis set limitations and poor scaling with their number. Explicit R12, F12 helps.)*
- *(No established multi-reference CC approach yet that can compete with single-reference CC..)*

All the problems that keep the DFT world busy, are automatically accommodated by WFT. So why not work *down* from the S eqn to correlated orbital theory models, including KS-DFT?

OUTLINE

1. Is it possible to get exact effective one-particle equations for orbitals (COT)
$$h^{\text{eff}}\varphi_p(1)=\varepsilon_p \varphi_p(1)$$
 from first principles ?
2. Is the Ip condition that $\Delta I_m = E(N-1)-E(N)$, where $\varepsilon_p \simeq -I(i)$ satisfied? The exact orbital dependent 'functional' of such a COT is then $E_C = \sum \langle ab || ij \rangle t_{ij}^{ab}$.
3. Can we approximately replace the non-local operators in COT with local ones as in KS-DFT?
4. Are the potentials generated qualitatively different than in GGA's, hybrids, etc?
5. If the Ip condition is satisfied for the potential, meaning the self-consistent orbitals and density are changed, does that pay dividends for energies and other properties?
6. What is the role of self-interaction in satisfying the Ip property?
7. Can the correlation potential be converged just as correlated, *ab initio* quantum chemistry can be for the wavefunction and all its properties?
8. RPA, the sum of just Coulomb ring diagrams in CCD is very popular in DFT., but few examples actually generate the self-consistent V_C (RPA). Our methods do this.
9. What is its effect on energies and Ip's?

Conclusions

1. Is it possible to get exact effective one-particle equations for orbitals?

$$h^{\text{eff}} \varphi_P(1) = \varepsilon_p \varphi_P(1) ?$$

$$\varepsilon_i = -I(i). \quad \varepsilon_a = A(a)$$

WAVE FUNCTION THEORY:

$$E = \text{Tr} f(p,q)\gamma(p,q) + \frac{1}{4}\text{Tr}\langle pq||rs\rangle\Gamma^c(p,q,s,r)$$

Ip-EOM-CC allows deriving a set of effective one-particle correlated orbital theory (COT) eqns,

$$(\mathbf{f} + \Sigma_{CC})\boldsymbol{\varphi}(i) = \epsilon(i)\boldsymbol{\varphi}(i),$$

where Σ_{CC} is a frequency independent 'self-energy' that can be exactly expressed in terms of CC amplitudes.

$\epsilon(i) = -I(i)$ which are exact principal Ip's.

RJB, "Towards an exact correlated orbital theory for electrons," Frontiers Article, Chem. Phys. Lett. 484, 1-9 (2009).

Method is required to fulfill this condition and that for EA's for unoccupied orbs.

What we do goes something like this...

One-particle operator \rightarrow

Brueckner Orbitals

The first two terms are $\langle a|f|i\rangle = f_{ai} = 0$ in HF.

Adding VR_0V starts to add correlation, V_C , so $h^{\text{eff}} = f + V_C$

Next step is to get the h^{eff} , and its orbital energies in COT, and show that the latter are principal I_p 's and E_a 's.

Standard Löwdin

P^- consists of hole determinants
all higher than

P^+ consists of particle determinants

Q^+ indicates

Note appearance
of

But such a frequency dependent form will not be the same for all orbitals! This is like the Dyson equation.

So instead of the part \hat{g}

This gives us two equations, one for the effective hamiltonian, G_{PP} , and the other for The R_{QP} operators in IP(EA)-EOM-CC...

This defines $\psi(\mathbf{r}, t)$ or $\psi(\mathbf{r}, E)$
eigenvalues are the EXACT

The correlation orbital potential in g, is....

+

It has two terms, one from the ground state correlation, t_{ij}^{ab} and the other deriving from new correlation for the ionized states, s_{kl}^{md} , but in such a way that they are the same for every *lp* or *Ea* when considering the unoccupied orbitals.

In second-order these terms become relative to HF orbitals...

Dyson-like terms, but frequency independent

**These are the extra terms that show up for
Brueckner or Kohn-Sham orbitals.....**

HARTREE-FOCK

= 0

CORRELATED ORBITAL THEORY

Now we know there is an exact, effective one-particle theory that has the property that it gives the exact principal I_p 's and E_a 's. Can DFT be viewed as an approximation to this exact theory?

DENSITY FUNCTIONAL THEORY:

$$E(\rho) = T_s - \int d\mathbf{1} v(\text{ext})\rho(\mathbf{1}) + \iint d\mathbf{1}d\mathbf{2}\rho(\mathbf{1})\rho(\mathbf{2}) + Exc[\rho]$$

$$\frac{\partial E}{\partial \rho} = h_s = t + v(\text{ext}) + J + Vxc$$
$$\epsilon(i) \approx -I(i)?$$

There are three inter-related quantities in KS-DFT.

The energy functional, the potential, usually defined as a derivative of the functional, and the density built from the KS orbitals. The latter can be no better than the potential. That is the weak link!

Our definition of a “consistent” DFT is one whose *functional* provides total energy properties accurately, and whose *potential* provides eigenvalues that are good approximations to *all* the principal Ip’s.

2. Is the Ip condition that

$$\Delta I_m = E_{\text{DFT}}(N-1) - E_{\text{DFT}}(N) \simeq \epsilon_m \text{ satisfied?}$$

Relationship of Potential to Orbital Energies, Ip's.

“ Given the auxiliary nature of the KS orbitals-just N orbitals the sum of squares of which add up to the true total electron density-one should expect no simple physical meaning for the Kohn-Sham orbitals energies. There is none. ”

Parr and Yang Book

“The individual eigenfunctions and eigenvalues, ϵ_j and ϕ_j , of the KS equations have no strict physical significance...”

W. Kohn, A. Becke, and R. G. Parr

“ Using TD-DFT in the adiabatic approximation, and simply the assumption that an electron is excited into the continuum, subject to a local kernel and using the fact that all integrals involving continuum and occupied orbitals vanish from A and B matrices, the eigenvalues of the KS equations using realistic OEP based potentials should approximately correspond to ionization potentials ”

R. J. Bartlett, V. F. Lotrich and I. V. Schweigert,

JCP, 2005

TDDFT (adiabatic) Eqns.

$$f_{\sigma\tau}(1,2) = \delta V_{XC}(2) / \delta \rho(1)$$

When you add a z (zero) fn to your basis set, it will take the place of a virtual orbital, a , with zero energy and zero overlap with any other function in the square-integrable basis set. Thus all integrals and $\epsilon_z = 0$, so the only terms left are the occupied orbital energies, ϵ_i . Therefore they must correspond to ionization potentials!

We actually use this trick to make an excited state EOM-CC program give results for ionized states, eg.

Others have reached similar conclusions differently.

D. P. Chong, O Gritsenko, E. V. Baerends, approximately related the KS-DFT eigenvalues to the solutions of Dyson's Eqn. showing that they included orbital relaxation and should be better than Koopmans'.(JCP, 2002.)

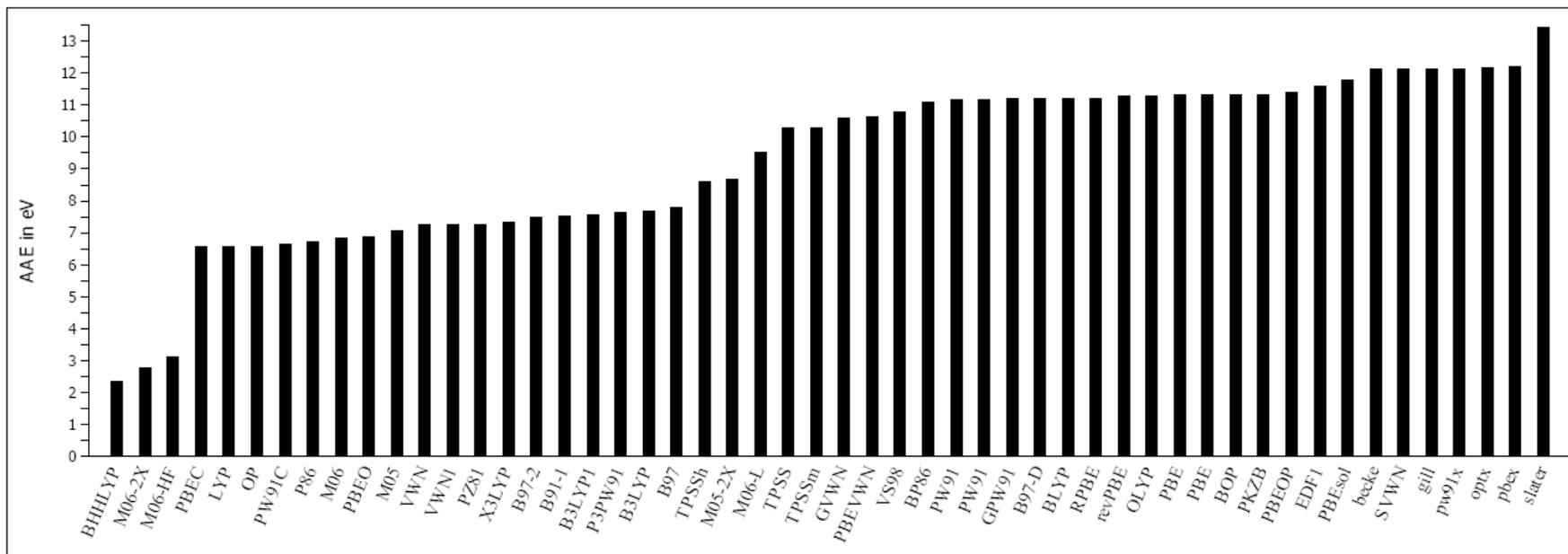
Hence, we expect the KS eigenvalues to correspond to principal ionization potentials for all orbitals, not just for the homo! When the potential ensures this and the functional provides total energies accurately, we define that as a 'Consistent' DFT.

None of the functionals being used today are consistent!

Do explicit density functionals satisfy this theorem?

$$\epsilon_i \sim -|P^{\text{exact}}$$

HF, HCN, N₂, C₂H₂, F₂, NH₃, H₂O, H₂CO, CH₄, C₂H₄

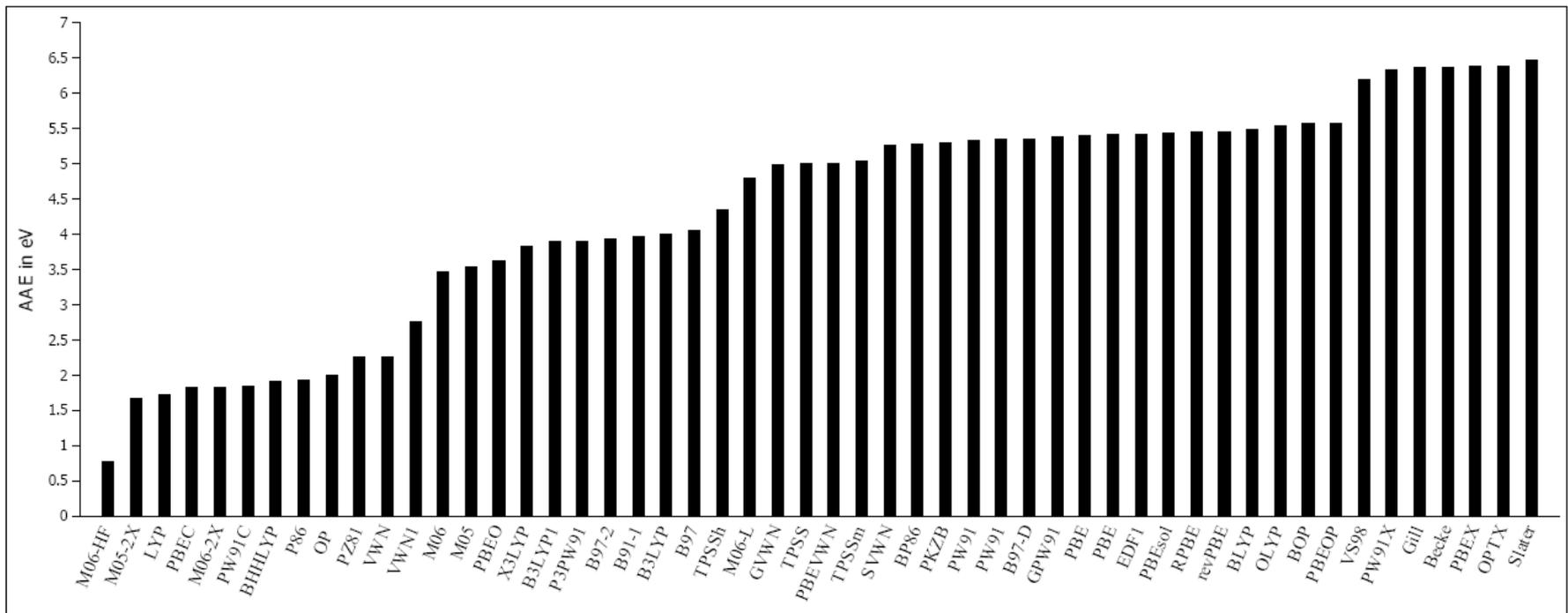


Performance of DFT potential for the characterization of the vertical ionization energies in eV as the negative of eigenvalues of the KS operator $(-\epsilon_i - I_i)$, $i \in$ all occupied orbitals)

How about the HOMO Condition?

$$\epsilon_{HOMO} = -IP^{exact}$$

HF, HCN, CO, N₂, C₂H₂, F₂, NH₃, H₂O, H₂CO, CH₄ and C₂H₄



Performance of DFT potential for the characterization of the vertical ionization energies in eV as the negative of eigenvalues of the KS operator ($(-\epsilon_i - I_i)$, $i \in \text{HOMO orbitals}$)

**Does any DFT method have this property?
And still provide accurate total energy properties?**

Yes, *ab initio dft*. This naturally corrects for self-interaction and for the long-range behavior of the functional.

Optimized Effective Potential for Exchange and Correlation

$$F_{\mu\nu}^{\text{exx+oep2-sc}} = h_{\mu\nu} + \sum_{\kappa\tau} P_{\kappa\tau}(\mu\nu|\kappa\tau) + (v_x^{\text{exx}})_{\mu\nu} + (v_c^{\text{ope2}})_{\mu\nu}$$

	$-\epsilon_i^{\text{exx+oep2}} - I_i$	$-\epsilon_{\text{core}}^{\text{exx+oep2}} - I_i$	$-\epsilon_{\text{valence}}^{\text{exx+oep2}} - I_i$	$-\epsilon_{\text{HOMO}}^{\text{exx+oep2}} - I_i$
Average Error	-5.67	-20.2	-0.12	-0.04
Average Absolute Error	5.67	20.2	0.85	0.31
Maximum Deviation	26.60	26.6	3.68	0.69
Minimum Deviation	0.0	16.01	0.00	0.00

Numerical evidence for the IP Theorem :

$$F_{\mu\nu}^{\text{hf+exx+oep2-sc}} = h_{\mu\nu} + \sum_{\kappa\tau} P_{\kappa\tau}(\mu\nu|\kappa\tau) + \frac{1}{2}(v_x^{\text{exx}})_{\mu\nu} + \frac{1}{2}(v_x^{\text{nlx}})_{\mu\nu} + (v_c^{\text{ope2}})_{\mu\nu}$$

	$-\epsilon_i^{\text{hf+exx+oep2}} - I_i$	$-\epsilon_{\text{core}}^{\text{hf+exx+oep2}} - I_i$	$-\epsilon_{\text{valence}}^{\text{hf+exx+oep2}} - I_i$	$-\epsilon_{\text{HOMO}}^{\text{hf+exx+oep2}} - I_i$
Average Error	-0.24	-0.89	-0.00	-0.04
Average Absolute Error	0.59	1.00	0.45	0.26
Maximum Deviation	2.25	2.25	1.78	0.66
Minimum Deviation	0.01	0.03	0.01	0.01

Importance of the non-local exchange in the KS operator.

3. Can we replace the non-local operators in COT with local ones as in KS-DFT?

That's how do we do *ab initio dft*.

Optimized Effective Potential

$$X(r_1, r_2) = 2 \sum \varphi_i^*(r_1) \varphi_a(r_1) \varphi_a^*(r_2) \varphi_a(r_2) / (f_{ii} - f_{aa})$$

Make Matrix Representation, \mathbf{X}

$\mathbf{XV}_x = \mathbf{Y}^{(1)}$ ($\mathbf{K}_i^a = \sum_j \langle aj|ji \rangle$; $\rho^{(1)} = 0$) **Exchange Only OEP.**
Functional is EXX = $-\frac{1}{2} \sum_{i,j} \langle ij|ji \rangle$, Potential, OEPx = OEP1

$\mathbf{XV}_c = \mathbf{Y}^{(2)}$ ($f_i^a, \langle ab|ij \rangle$; $\rho^{(2)} = 0$)
Correlation Functional is E_2 from MBPT2 ,

 $I \langle J, A \rangle_B (2 \langle IJ|AB \rangle - \langle IJ|BA \rangle) \langle IJ|AB \rangle / (f_{ii} - f_{JJ} + f_{AA} + f_{BB})$

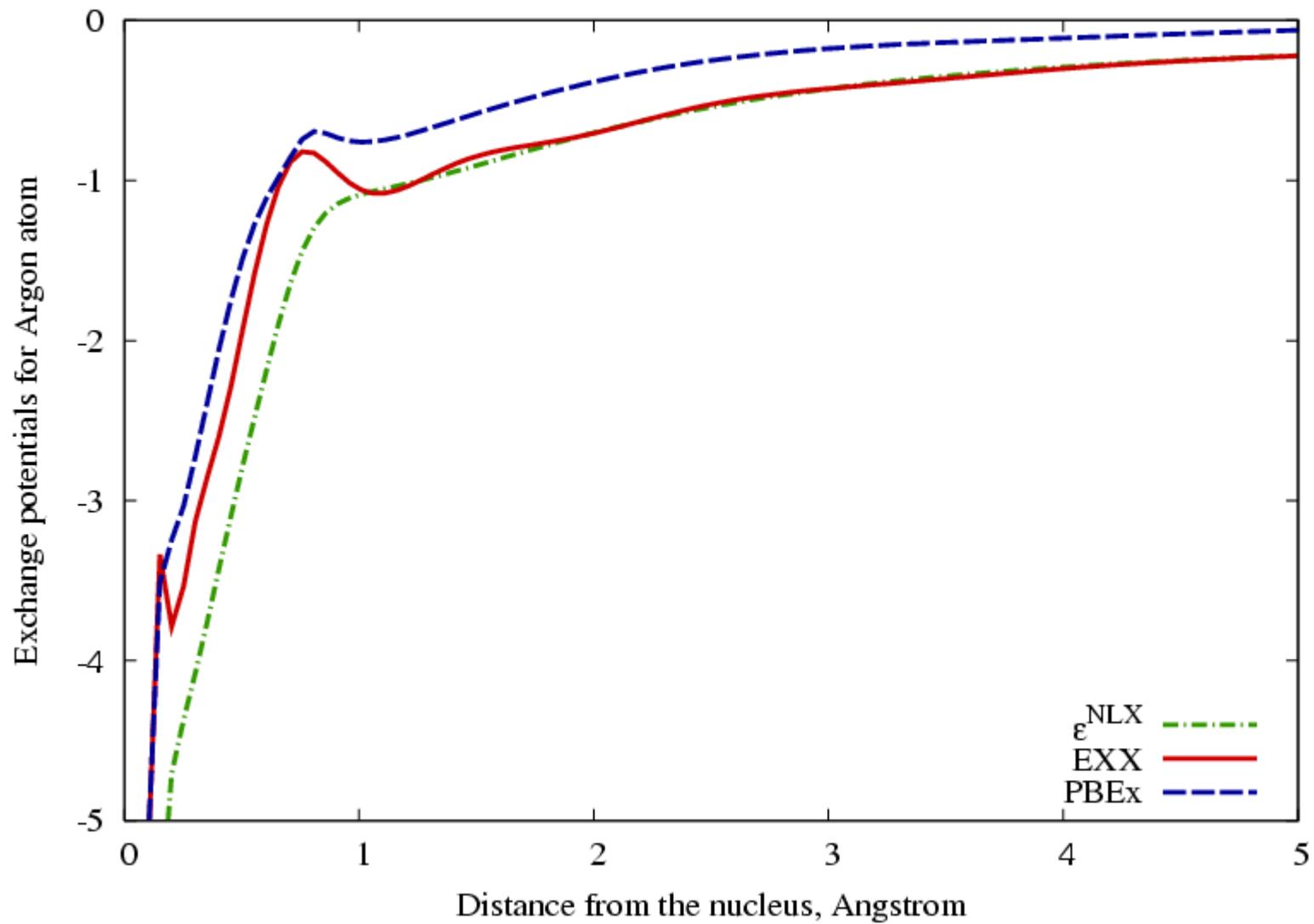
$+ 2 \langle I, A \rangle_{I,A} |\langle I|f|A \rangle|^2 / (f_{ii} - f_{AA}) + \dots$ **Potential is OEP2sc.**

$\mathbf{XV}^{(2)}_{xc} = \mathbf{Y}^{(1+2)}$ ($\mathbf{K}_i^a, f_i^a, \langle ab|ij \rangle$; ; $\rho^{(1+2)} = 0$),
 X^{-1} uses generalized inverse from SVD

Insert $\mathbf{V}^{(2)}_{xc}$ in KS eqns, and iterate to self-consistency.

If want a higher approximation like RPA, linCCD, CCD, CCSD, ...
 Can do in the same way by adjusting the right-hand $\mathbf{Y}^{(\infty)}$, and $\rho^{(\infty)} = 0$

4. Are the potentials generated any different than PBE, eg?



NOW FOR CORRELATION.

Now for the OEP (Optimized Effective Potential) for correlation...

1. Take orbital-dependent correlation function from wave-function theory (MBPT-2, CC, RPA, etc).
2. Impose the density condition that the KS determinant has to provide the correct, correlated density to unambiguously define V_{xc}
3. However, the method requires an $H=H_0+V$ where V is a well-behaved correlation perturbation. Our semi-canonical choice is contrary to that used in DFT circles.
4. Employ the response function in matrix representation, X , to define the eqns to be solved.
5. Solve them using a generalized inverse (SVD) for the X .

Semi-canonical Choice : $(\hat{H}_0)_N = \sum_p f_{pp}\{p^\dagger p\} + \sum_{i \neq j} f_{ij}\{i^\dagger j\} + \sum_{a \neq b} f_{ab}\{a^\dagger b\}$

GMBPT-Self-interaction free

$$\hat{V}_N = \sum_{i,a} f_{ai}[\{a^\dagger i\} + \{i^\dagger a\}] + W ,$$

Kohn-Sham Choice :

$$V' = V + \sum_p \langle p | \hat{v}^{HF} - \hat{u} | p \rangle \{p^\dagger p\} + \sum_{i \neq j} \langle i | \hat{v}^{HF} - \hat{u} | j \rangle \{i^\dagger j\} + \sum_{a \neq b} \langle a | \hat{v}^{HF} - \hat{u} | b \rangle \{a^\dagger b\}.$$

Has diagonal and other large one-particle terms in V

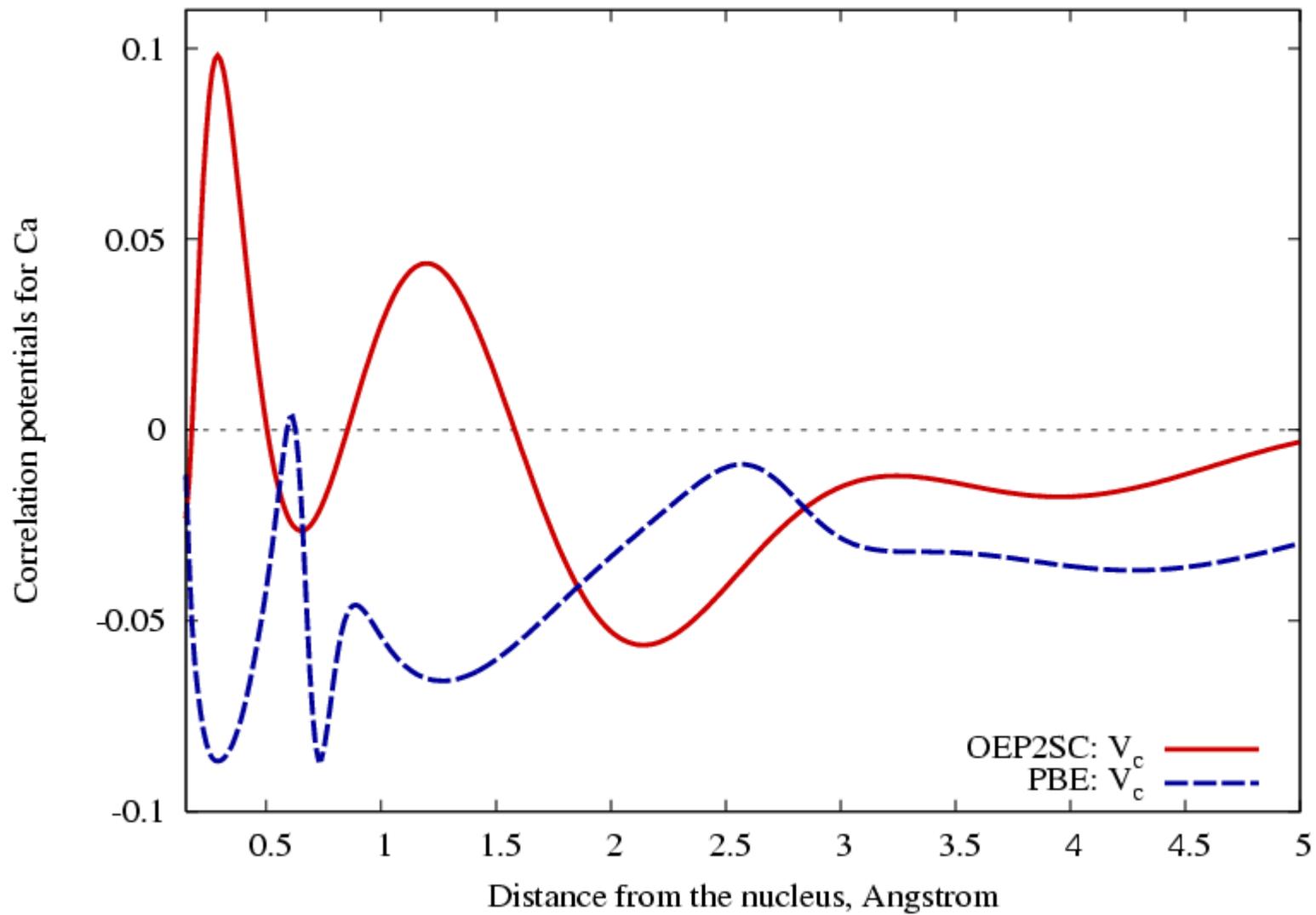
$$\begin{aligned}
\phi_a \phi_i^* \hat{V}_c / d_{ia} + c.c. &= \phi_a \phi_i^* \left[\frac{1}{2} \sum_{jcb} t_{ij}^{cb} \langle aj || cb \rangle / d_{ia} + c.c. \right. \\
&\quad - \frac{1}{2} \sum_{kjb} t_{kj}^{ab} \langle kj || ib \rangle / d_{ia} - c.c. \\
&\quad + \sum_{jb} t_{ij}^{ab} \langle j | \hat{K} - \hat{V}_{\text{exx}} | b \rangle / d_{ia} + c.c. \\
&\quad \left. + \sum_{jb} \langle aj || ib \rangle \langle b | \hat{K} - \hat{V}_{\text{exx}} | j \rangle / d_{jb} d_{ia} + c.c. \right]
\end{aligned}$$

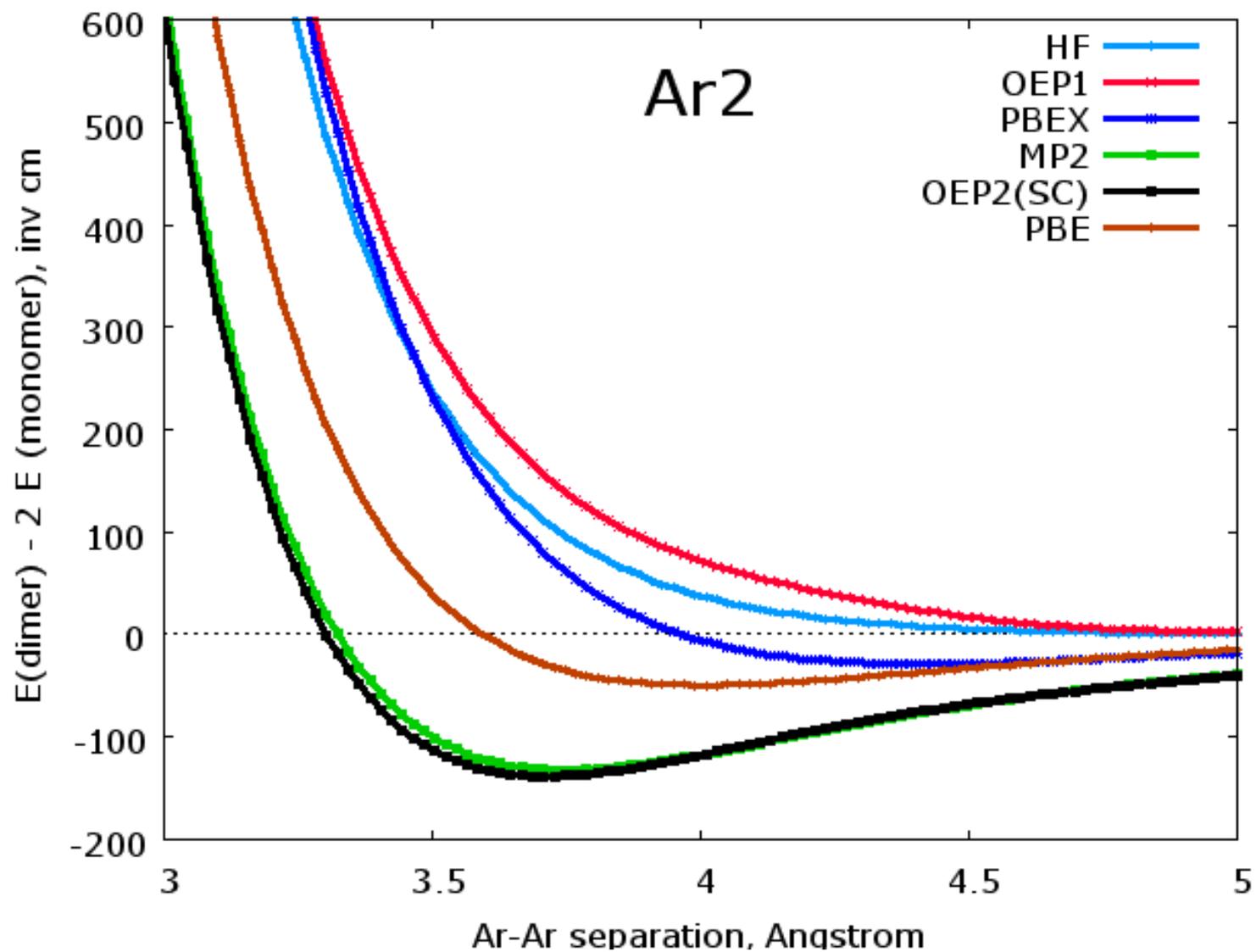
Real Space! !

$$\begin{aligned}
&+ \sum_{jb} t_{ij}^{ab} \langle j | \hat{K} - \hat{V}_{\text{exx}} | b \rangle / d_{jb} + c.c.] \\
&+ \phi_a^* \phi_b [\langle i | \hat{V}_{\text{HF}} - \hat{V}_{\text{exx}} | a \rangle \langle b | \hat{V}_{\text{HF}} - \hat{V}_{\text{exx}} | i \rangle / d_{ib} d_{ia} \\
&+ \sum_{ijc} \frac{1}{2} t_{ij}^{ca} t_{ij}^{cb}] \\
&- \phi_i^* \phi_j [\langle j | \hat{V}_{\text{HF}} - \hat{V}_{\text{exx}} | a \rangle \langle a | \hat{V}_{\text{HF}} - \hat{V}_{\text{exx}} | i \rangle / d_{ia} d_{ja} \\
&+ \frac{1}{2} \sum_{kab} t_{ab}^{kj} t_{ki}^{ab}] ,
\end{aligned}$$

Table 1. Total energies (au))

AAE (KJ/mol)	MP2 58.2	OEP2-ks KS Choice	OEP2-sc 26.7	PBE 36.2	CCSD(T)
N ₂	-109.44914	-109.74806	-109.45777	-109.45707	-109.46861
N ₂ ⁺	-108.88633	No conv	-108.90544	-108.89077	-108.90055
N	-54.544740	-54.593111	-54.545199	-54.535569	-54.564854
H ₂ O	-76.370003	-76.510744	-76.373092	-76.369991	-76.383576
H ₂ O ⁺	-75.901155	-75.989525	-75.902958	-75.912146	-75.921765
CN	-92.598196	No conv	-92.651919	-92.646898	-92.658287
CN ⁻	-92.772714	No conv	-92.780718	-92.783715	-92.796498
CO	-113.22852	No conv	-113.23781	-113.23959	-113.25124
CO ⁺	-112.70221	No conv	-112.73481	-112.72994	-112.73989
O ₂	-150.20577	No conv	-150.22187	-150.25505	-150.22156
Ne	-128.85959	-128.95144	-128.86117	-128.86584	-128.86513
Ne ⁺	-128.06679	No conv	-128.06757	-128.06871	-128.08020





Arguments for OEP based upon MBPT2 and LinCCD (*ab initio dft*)

$$E(\textit{ab initio dft}) = T^S + V^{\text{ext}} + E^H + E^X + E^C$$

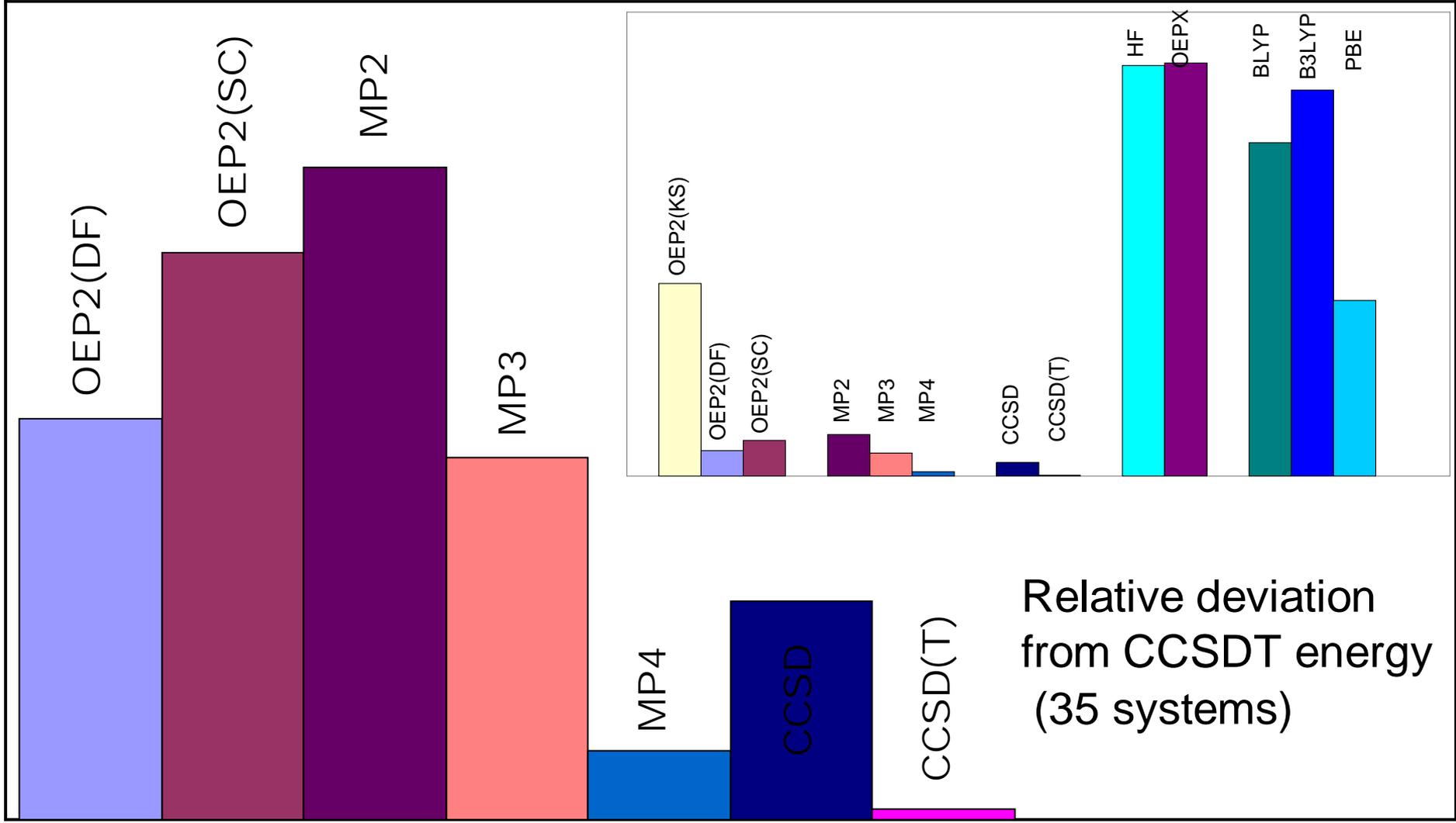
$$E^C = E^C(\text{GMBPT2})$$

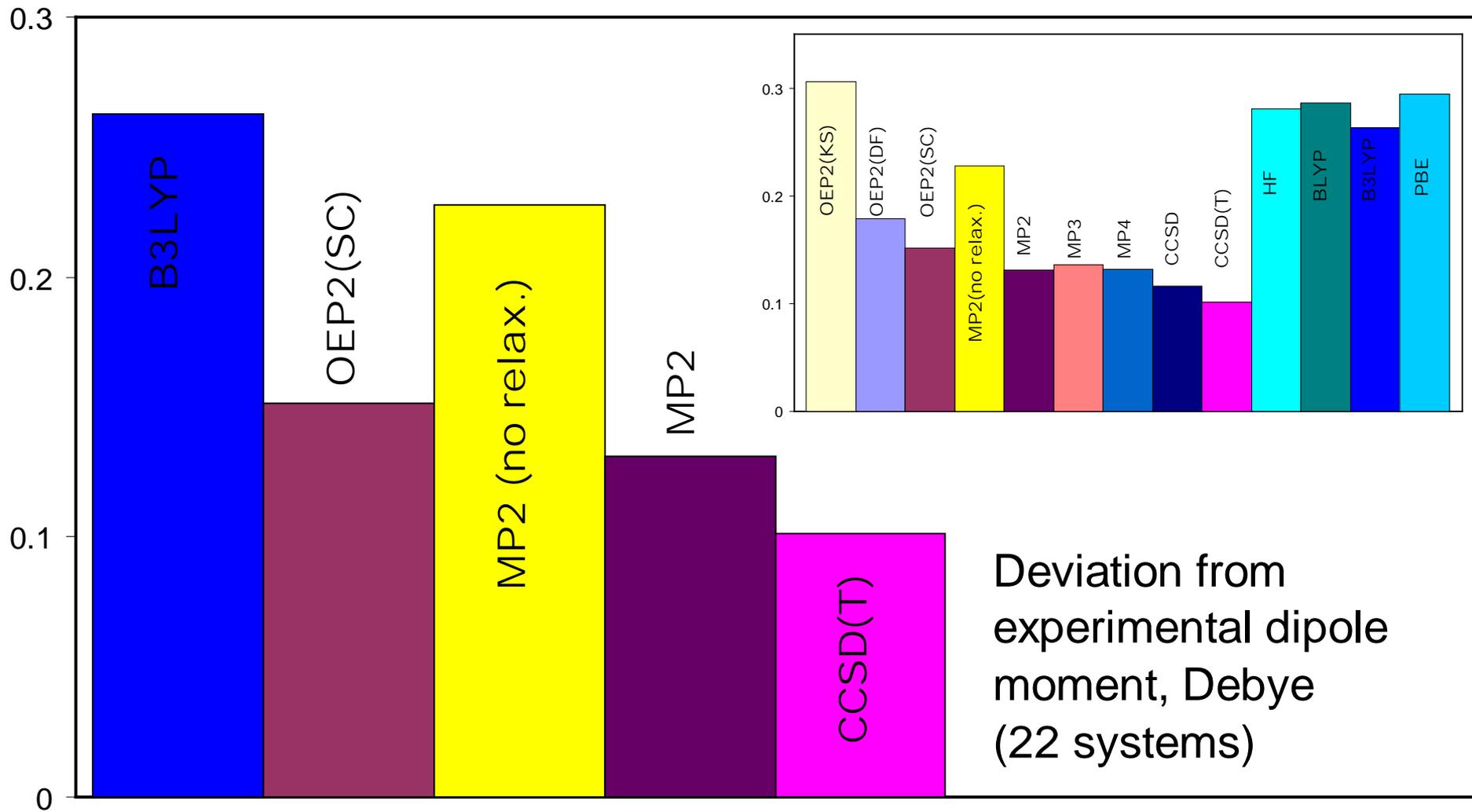
$$E^C = E^C(\text{LinCCD})$$

All functionals are orbital dependent, and thus non-local. Potentials, V_{XC} , are local.

- Functional includes exact exchange, which eliminates self-interaction errors.
- KS based PT fails miserably for correlation. $V_{XC} = \text{OEP2sc}$ fixes the problem.
- $E(\text{OEP2sc})$ is rigorously correct in the high-density limit.
- The LinCCD extension is a non-perturbative, infinite-order generalization.
- Hermitian.
- Orbital energies provide excellent approximations to all-valence ionization potentials.
- Adding 50% K to 50% $V_X(\text{OEP2sc})$ provide excellent core ionization potentials.
- A KS method that is **fully consistent**, in that it provides both excellent total energy properties (**better than MP2**) and a V_{XC} that gives ionization potentials as the **eigenvalues** of the KS system.
- Provides dispersion interactions as a natural consequence of KS-DFT.

5. If the I_p condition is satisfied for the potential, meaning the orbitals and density are changed, does that pay dividends for energies and other properties?





6. What is the role of self-interaction in satisfying the lp property?

Why does *ab initio* dft have to give the right Koopmans' Ip's?

The functional is....

$$E(\text{neutral}) = \sum_i \langle i | h | i \rangle + \frac{1}{2} \sum_{i,j} \langle ij || ij \rangle + E_C \quad \text{No SIE.}$$

$$E(\text{cation}) = \sum_{i \neq m} \langle i | h | i \rangle + \frac{1}{2} \sum_{i,j \neq m} \langle ij || ij \rangle + E_C(\neq m)$$

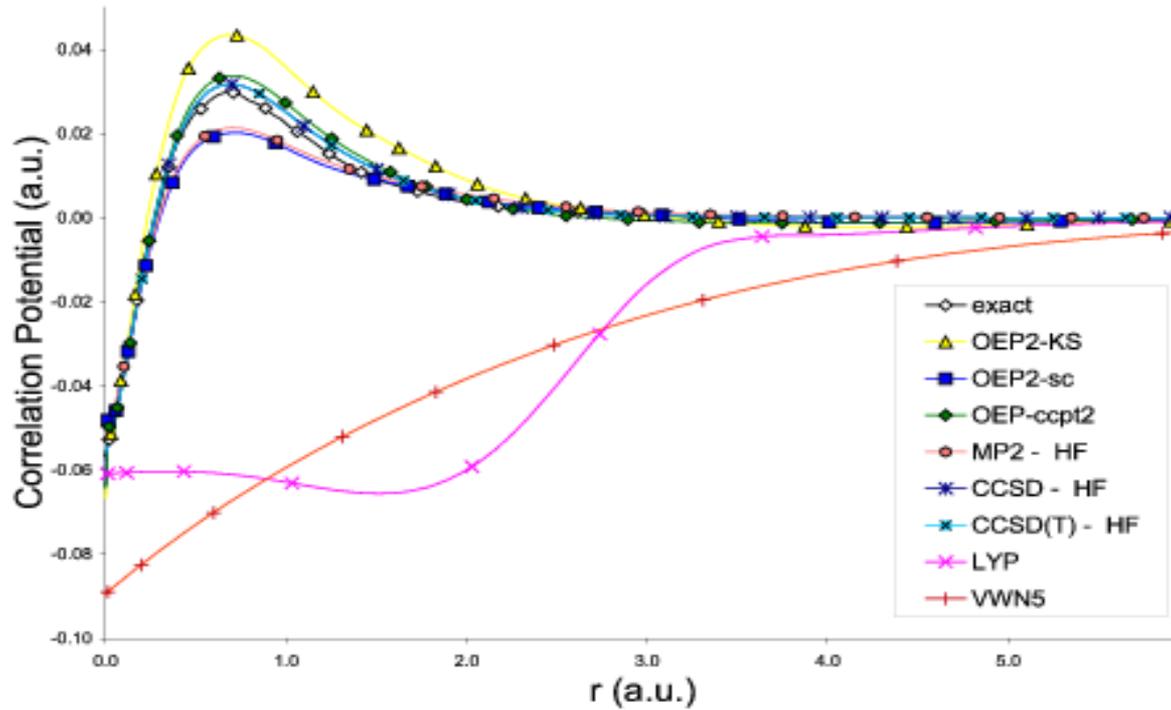
$$E(\text{cation}) - E(\text{neutral}) = I(m)!$$

If the potential generated from the OEP procedure is faithful to the energy functional, our Ip proof requires that...

$$h^{\text{eff}} \varphi_m = (t + v_{\text{ext}} + J + V_X^{\text{OEP}} + V_C^{\text{OEP}}) \varphi_m = \varepsilon_m \varphi_m$$

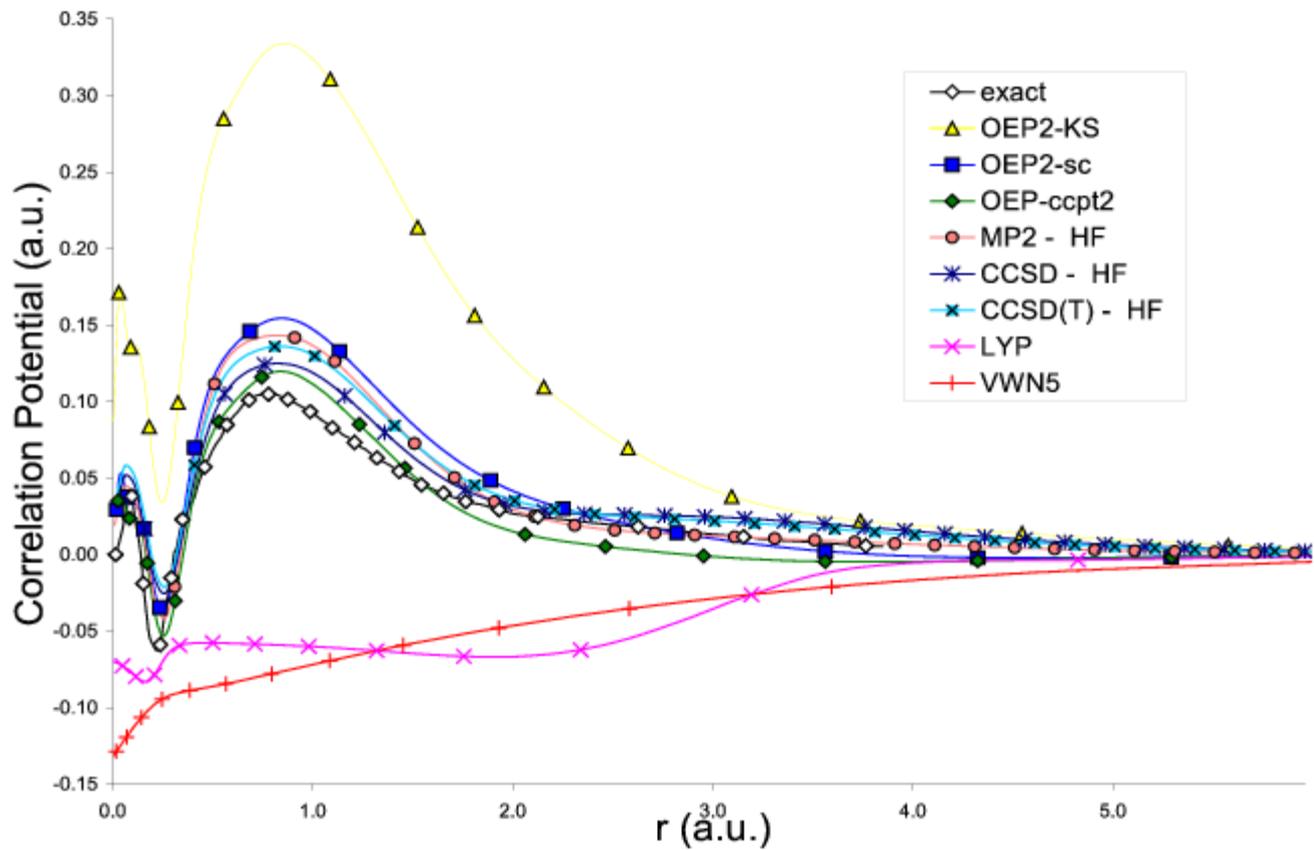
$$I(m) \simeq -\varepsilon_m$$

7. Can the correlation potential be converged just as correlated, *ab initio* quantum chemistry can be for the wavefunction and all its properties?

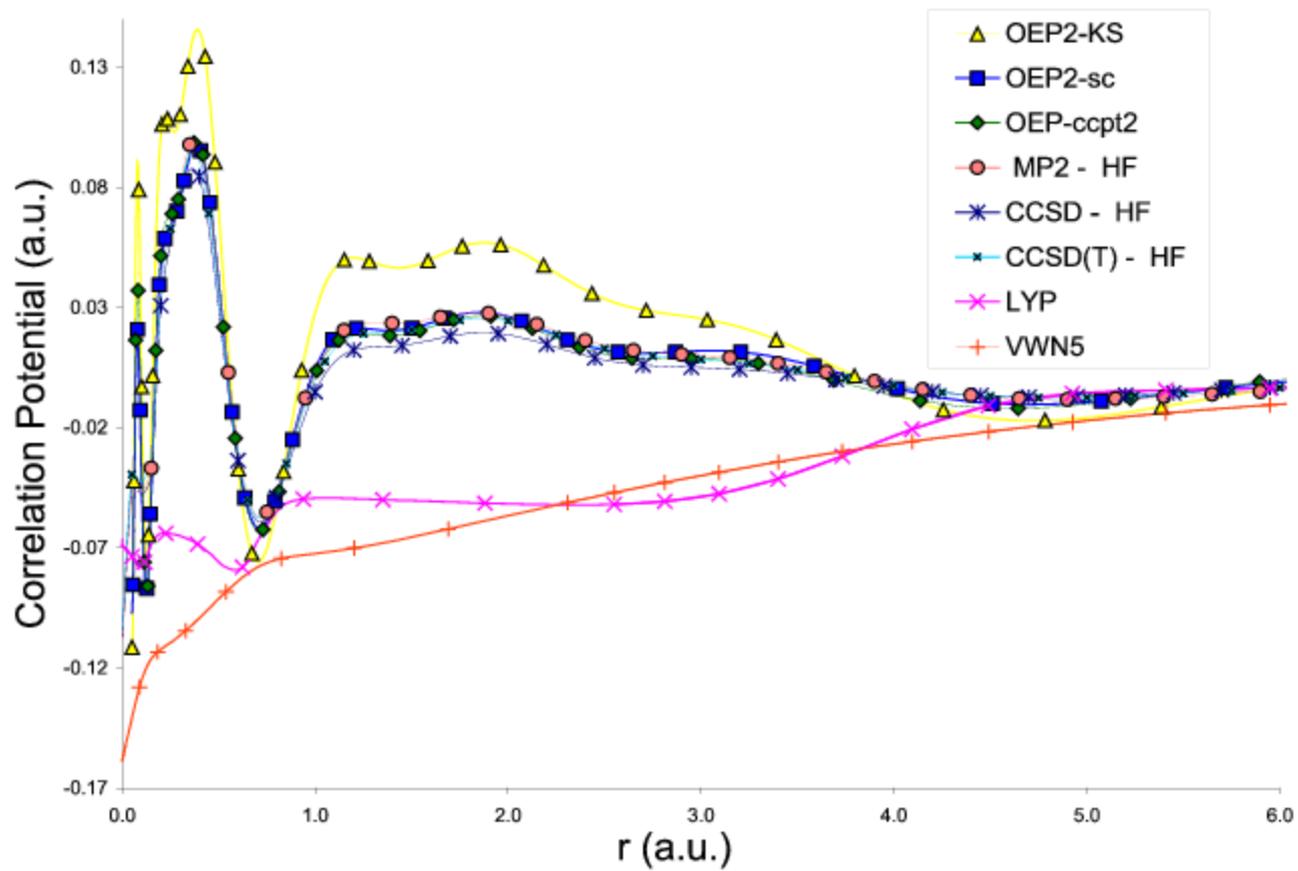


He Correlation Potentials

Irek Grabowski, A. M. Teal, S. Smiga, K. Jankowski, R. J. Bartlett,
JCP, 2011..



Ne Correlation Potential



Ar Correlation Potential

8. RPA, the sum of just Coulomb ring diagrams in CCD is very popular in DFT, but few examples actually generate the self-consistent $V_C(\text{RPA})$. What is its effect on energies and Ip's?

ANOTHER APPROACH

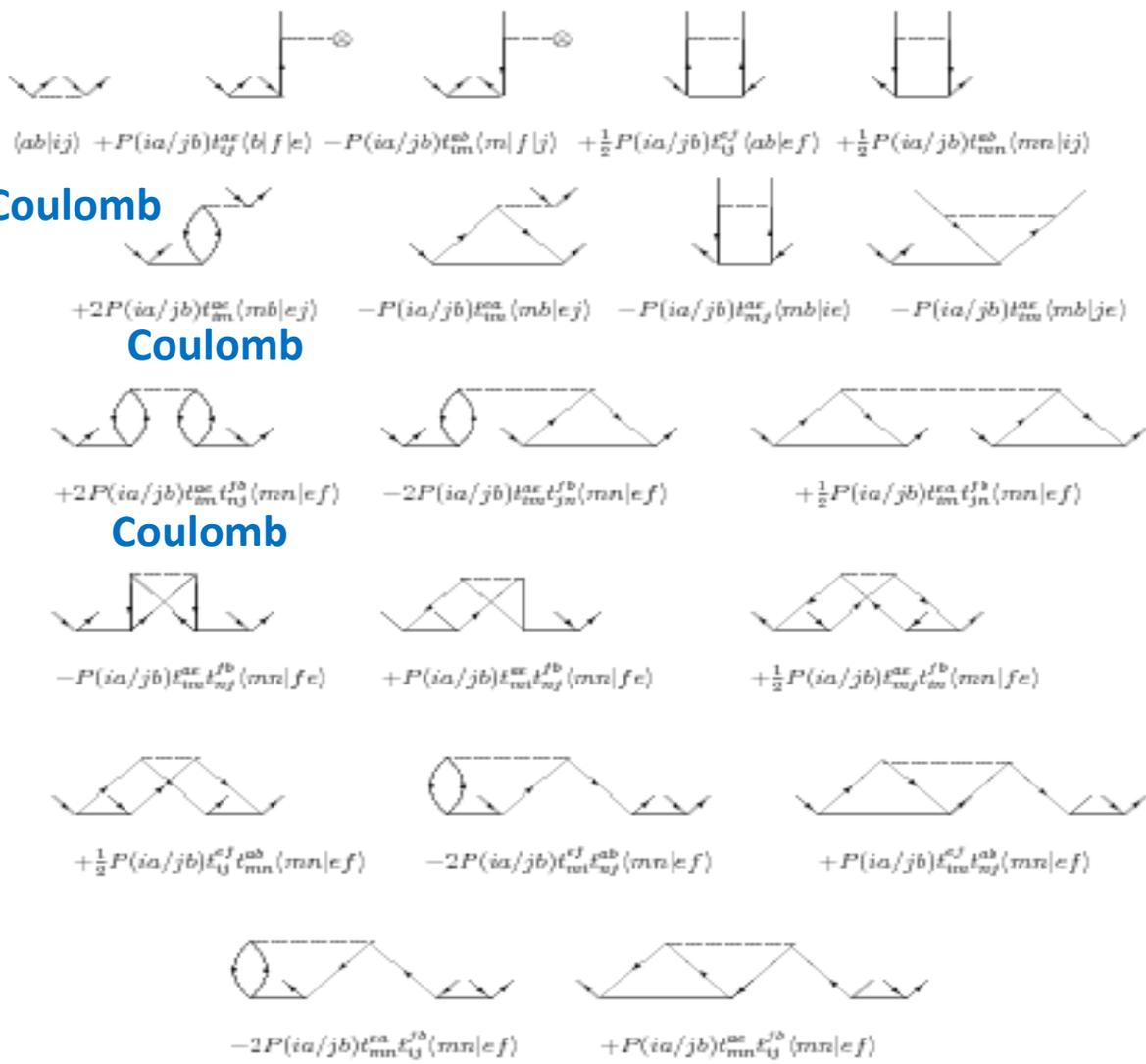
Functionals from Adiabatic connection/fluctuation-dissipation framework

$$E_{xc}^{Exact} = \frac{1}{2} \int_0^1 d\lambda \int d\vec{r} \int d\vec{r}' \frac{1}{|\vec{r} - \vec{r}'|} \left[-\frac{1}{\pi} \int_0^\infty d\omega \chi_\lambda(\vec{r}, \vec{r}', i\omega) - \delta^3(\vec{r} - \vec{r}') \rho(\vec{r}) \right]$$

Problems:

1. Deal with coupling constant and frequency integration.
2. Solve Dyson type equation : $\chi_\lambda(\vec{r}, \vec{r}', i\omega) = \chi_0(\vec{r}, \vec{r}', i\omega) + \chi_0(\vec{r}, \vec{r}', i\omega) * (\lambda v_{ee} + f_{xc,\lambda}) * \chi_\lambda(\vec{r}, \vec{r}', i\omega)$
3. Deal with the kernel. **But RPA is the first approximation.**
4. Corresponding xc-potentials are difficult to construct makes SCF KS calculation computationally very demanding.
5. Post SCF implementations pose the problem of best reference orbitals.
6. Since, the exact analytical form of the kernel is unknown, going to the next hierarchy in approximation is not very straight forward.

But we can avoid any coupling-constant and frequency integration by simply taking the RPA expression from wavefunction theory, as the Coulomb-only sum of ring diagrams in CCD, and inserting them into our eqns for the density condition, just as we did with MBPT2, to define self-consistent potentials.



Goldstone diagrams for T_2 using doubly occupied spatial orbitals.

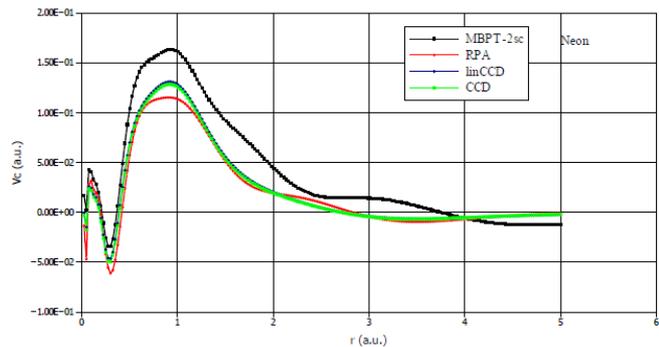
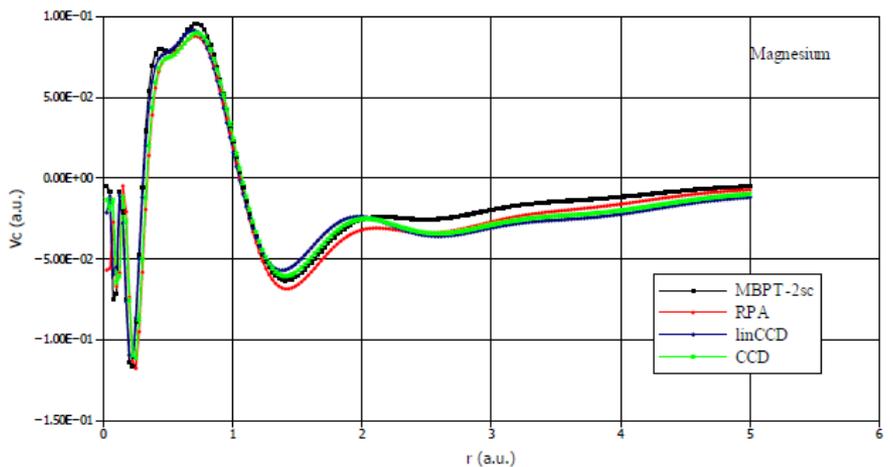
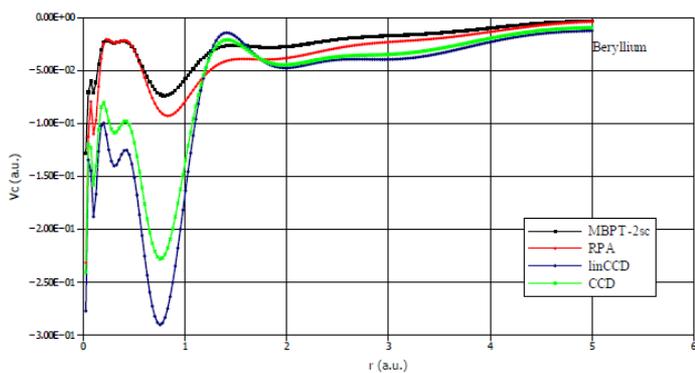
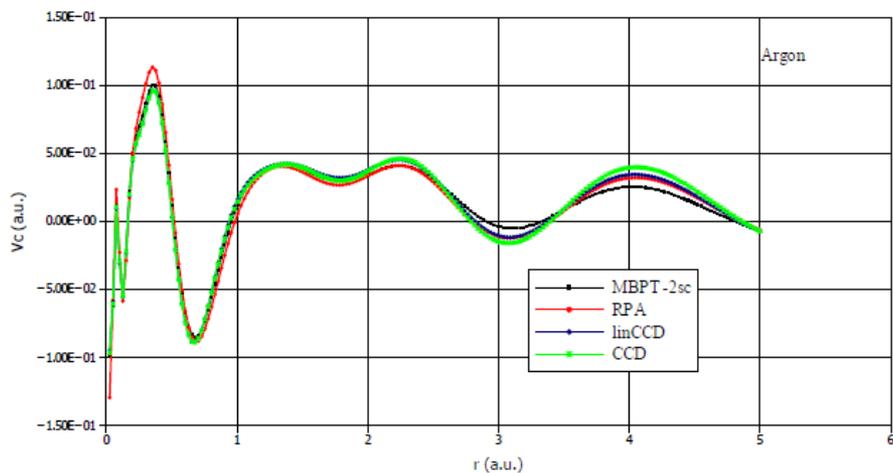
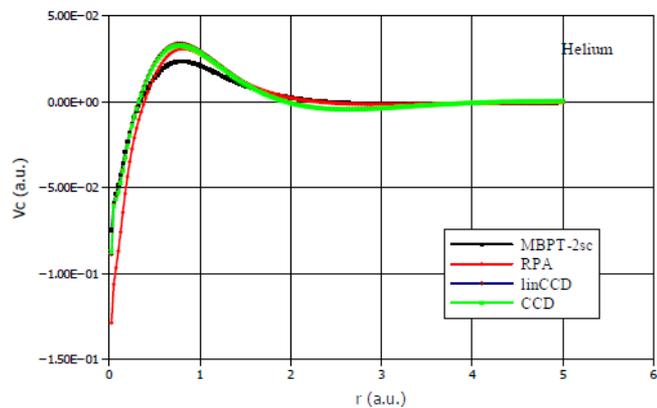
RPA Eqns from CC viewpoint.

The diagram shows an equation with four terms on the left and an equals sign followed by a zero on the right. The terms are:

- 1. A vertex with two incoming lines from the left and two outgoing lines to the right. A dashed line connects the two left vertices.
- 2. A vertex with two incoming lines from the left and two outgoing lines to the right. A loop is formed by a solid line on the left and a dashed line on the right, with an incoming line from the top.
- 3. A vertex with two incoming lines from the left and two outgoing lines to the right. A vertical solid line on the left is connected to a horizontal dashed line on the right, which ends in a circle with an 'X' inside.
- 4. A vertex with two incoming lines from the left and two outgoing lines to the right. Two loops are formed by solid lines on the left and dashed lines on the right, connected by a dashed line at the top.

$= 0$

Correlation potential due to RPA (ring-CCD) and beyond RPA (ring-CCD) such a lin-CCD, CCD



Arguments for RPA Treatment of Correlation

$$E^{\text{RPA}} = T^{\text{S}} + V^{\text{ext}} + E^{\text{H}} + E^{\text{X}} + E^{\text{CRPA}}$$

Coulomb Attenuation: The largest single perturbation is the Coulomb one. Sum it first to all orders, and then other terms might be treated with PT.

- Method uses exact exchange, which eliminates self-interaction errors.
- The RPA extension is a non-perturbative, infinite-order generalization that reduces to MBPT2 in the high-density limit.
- It is finite for metallic systems.
- It is size-extensive.
- RPA yields molecular interaction energies in the coupled- KS monomer level for large intermolecular separations.
- Correct for the high-density electron gas, meaning that the long-range interactions are properly included.
- Hermitian

And back to Koopmans' Thm--

Ionization Potentials for all Orbitals in Molecules (ev)

Molecules	Expt ^{63,68}	$-\epsilon^{2^{nd}}$	$-\epsilon_i^{oepr2-sc}$	$-\epsilon_i^{RPA}$	$-\epsilon_i^{lin-CCD}$	$-\epsilon_i^{CCD}$	IP-EOM-CCSD	IP-EOM-MBPT(2)
<i>HF</i>	16.19	14.20	15.33	16.36	16.07	16.11	15.96	15.93
	19.9	18.66	19.10	20.09	19.84	19.86	19.94	19.98
	39.6	36.91	38.48	39.56	39.26	39.29	39.22	39.11
<i>H₂O</i>	694.18	680.06	691.68	691.83	691.88	691.88	695.71	696.00
	12.62	11.13	11.97	12.82	12.49	12.54	12.51	12.53
	14.72	13.46	14.16	14.99	14.69	14.73	14.74	14.73
	18.51	18.03	18.08	18.93	18.63	18.66	19.03	18.98
	32.51	30.19	32.59	33.48	33.15	33.19	32.67	32.61
<i>NH₃</i>	539.7	527.76	538.59	538.53	538.58	538.59	541.41	541.84
	10.8	9.98	10.19	10.78	10.37	10.45	10.79	10.80
	16.8	15.82	15.55	16.19	15.78	15.85	16.55	16.50
	27.7	29.09	27.44	28.08	27.66	27.74	27.74	27.67
	405.6	397.52	404.53	404.42	404.3	404.39	406.99	407.4 5
Absolute Average Error		3.45	0.88	0.63	0.59	0.55	0.48	0.58

If you do everything comparatively right in DFT (ie *ab initio dft*)---what have we learned?

- Potentials have the correct shell structure and formally the correct asymptotic behavior.
- Self-interaction is properly handled.
- Dispersion interactions are correctly described.
- **DFT orbital energies are given meaning by an analog of Koopmans' approximation for *all* ionization potentials, but for relaxed orbitals.**
- There is no integer discontinuity problem.
- Results are usually better than that of standard DFT, and are in many cases competitive with coupled-cluster theory, even when using only a MBPT(2) functional.
- **Using higher-order coupled-cluster functionals further improves the potentials, demonstrating convergence.**

CONCLUSIONS

1. It is possible to get exact effective one-particle equations for orbitals (COT)

$$h^{\text{eff}}\varphi_p(1)=\varepsilon_p \varphi_p(1)$$

2. The Ip condition that $\Delta I_m = E_{\text{XC}}(N-1) - E_{\text{XC}}(N)$, where $\varepsilon_p = -I(i)$ is satisfied. The exact orbital dependent 'functional' of such a COT is then $E_{\text{XC}} = \sum \langle ab || ij \rangle t_{ij}^{ab}$..

3. To a good approximation we can replace the non-local operators in COT with local ones as in KS-DFT, but the functional should remain non-local.

4. The potentials generated are dramatically different than in PBE. (or any other choice.)

5. When the Ip condition is satisfied for the potential the theory gives improved results for energies and other properties.

6.. Correct self-interaction is critical in satisfying the Ip property.

7. The correlation potential shows convergence with level of theory, MBPT2, RPA, LinCCD, CCSD, CCSD(T), as does correlated, *ab initio* quantum chemistry.

8. RPA self-consistent correlation potentials were generated from the KS density condition, showing similar shape to other correlated theories and providing accurate results for ionization potentials as eigenvalues, even though RPA does not correspond to a correct Fermion wavefunction. Using RPA to attenuate the Coulomb interaction, makes other corrections like exchange and subsequent correlation smaller.

Many-Body Methods in Chemistry and Physics

MBPT and Coupled-Cluster Theory

Isaiah Shavitt and Rodney J. Bartlett

CAMBRIDGE MOLECULAR SCIENCE

The diagram shows the expansion of the many-body potential V and its powers V^2 and V^3 using many-body perturbation theory (MBPT) diagrams. The diagrams are arranged in three rows, each representing a different order of the expansion. The first row shows the expansion of V into one-body, two-body, and three-body terms. The second row shows the expansion of V^2 into terms involving two-body and three-body interactions. The third row shows the expansion of V^3 into terms involving two-body and three-body interactions. The diagrams are drawn with lines representing particles and vertices representing interactions, and they are arranged in a way that shows the hierarchical structure of the expansion.

$$V = V_1 + V_2 + V_3 + V_4 + V_5 + V_6 + V_7$$
$$V^2 = V_1^2 + V_1 V_2 + V_2 V_1 + V_1 V_3 + V_3 V_1 + V_2^2 + V_2 V_3 + V_3 V_2 + V_2 V_4 + V_4 V_2 + V_3^2 + V_3 V_4 + V_4 V_3 + V_2 V_5 + V_5 V_2 + V_3 V_6 + V_6 V_3 + V_4 V_7 + V_7 V_4$$
$$V^3 = V_1^3 + V_1^2 V_2 + V_2 V_1^2 + V_1 V_2 V_1 + V_1 V_3 V_1 + V_1 V_4 V_1 + V_2 V_1 V_2 + V_2 V_1 V_3 + V_3 V_1 V_2 + V_3 V_1 V_3 + V_2 V_2 V_1 + V_2 V_2 V_2 + V_2 V_2 V_3 + V_2 V_3 V_2 + V_2 V_3 V_3 + V_3 V_2 V_1 + V_3 V_2 V_2 + V_3 V_2 V_3 + V_3 V_3 V_1 + V_3 V_3 V_2 + V_3 V_3 V_3 + V_4 V_1 V_2 + V_4 V_1 V_3 + V_4 V_2 V_1 + V_4 V_2 V_2 + V_4 V_2 V_3 + V_4 V_3 V_1 + V_4 V_3 V_2 + V_4 V_3 V_3 + V_5 V_1 V_2 + V_5 V_1 V_3 + V_5 V_2 V_1 + V_5 V_2 V_2 + V_5 V_2 V_3 + V_5 V_3 V_1 + V_5 V_3 V_2 + V_5 V_3 V_3 + V_6 V_1 V_2 + V_6 V_1 V_3 + V_6 V_2 V_1 + V_6 V_2 V_2 + V_6 V_2 V_3 + V_6 V_3 V_1 + V_6 V_3 V_2 + V_6 V_3 V_3 + V_7 V_1 V_2 + V_7 V_1 V_3 + V_7 V_2 V_1 + V_7 V_2 V_2 + V_7 V_2 V_3 + V_7 V_3 V_1 + V_7 V_3 V_2 + V_7 V_3 V_3$$

CAMBRIDGE

