UNEDF- PACK FOREST

Ab-initio dft: The seamless connection with wave-function theory

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Non-local correlated orbital potentials (COP)

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$ AFOSR $

Ultimate objective: **Quantitative and qualitative determination of everything we want to know about molecules and their interactions from solutions of the Schroedinger (Dirac) equation.**

Includes:

- Structure.
- Vibrational, electronic, photoelectron, ESR, and NMR spectra.
- Activation barriers and transition states.
- Forces on potential energy surfaces to drive QM based MD

Cannot do this with sufficient accuracy without the effects of electron correlation...

TWO ROUTES TOWARD ELECTRON CORRELATION IN QUANTUM CHEMISTRY

I. **Effective one-particle theory:**
Density Functional Theory (and others like Dyson, etc.)

II. **Explicit n-particle (2-particle theory):**
Coupled-cluster theory

ROUTE II. AB INITIO, CORRELATED, SIZE EXTENSIVE WAVEFUNCTION METHODS COMBINED WITH CONVERGING BASIS SETS HAVE ...

Established the now widely used paradigm for ground state *Ab Initio* Calculations---

MBPT(2)<CCD <CCSD<CCSD[T] <CCSD(T) <CCSDT-1

1978 1982 1985 1989 1984

<CCSDT<CCSDT(Q_f) <CCSDTQ<**CCSDTQP** <FULL CI

1987 1998 1992 2002

Evolving Paradigm for CC/MBPT Approaches for Excited (Ionized, Electron Attached) States ---

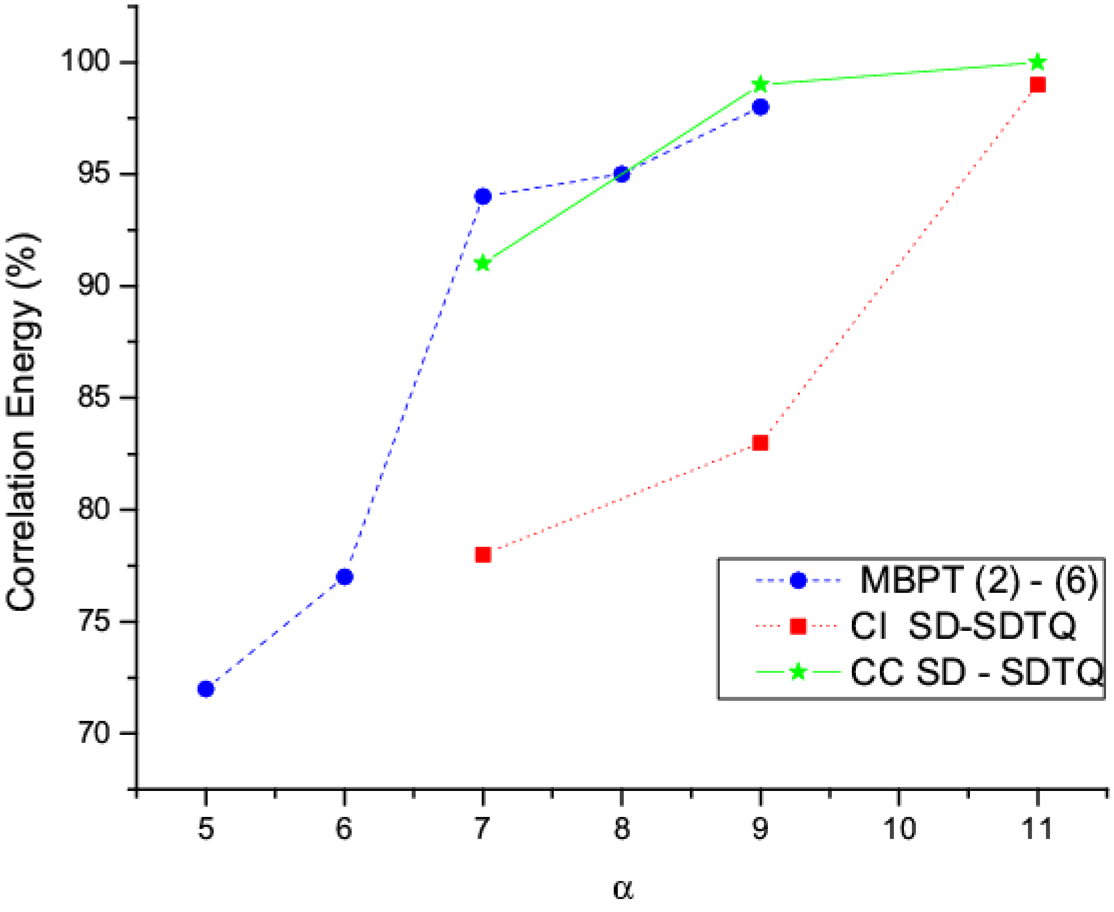
EOM-MBPT(2) <EOM-CCSD<STEOM-CC

1996 1984, 1993 1997

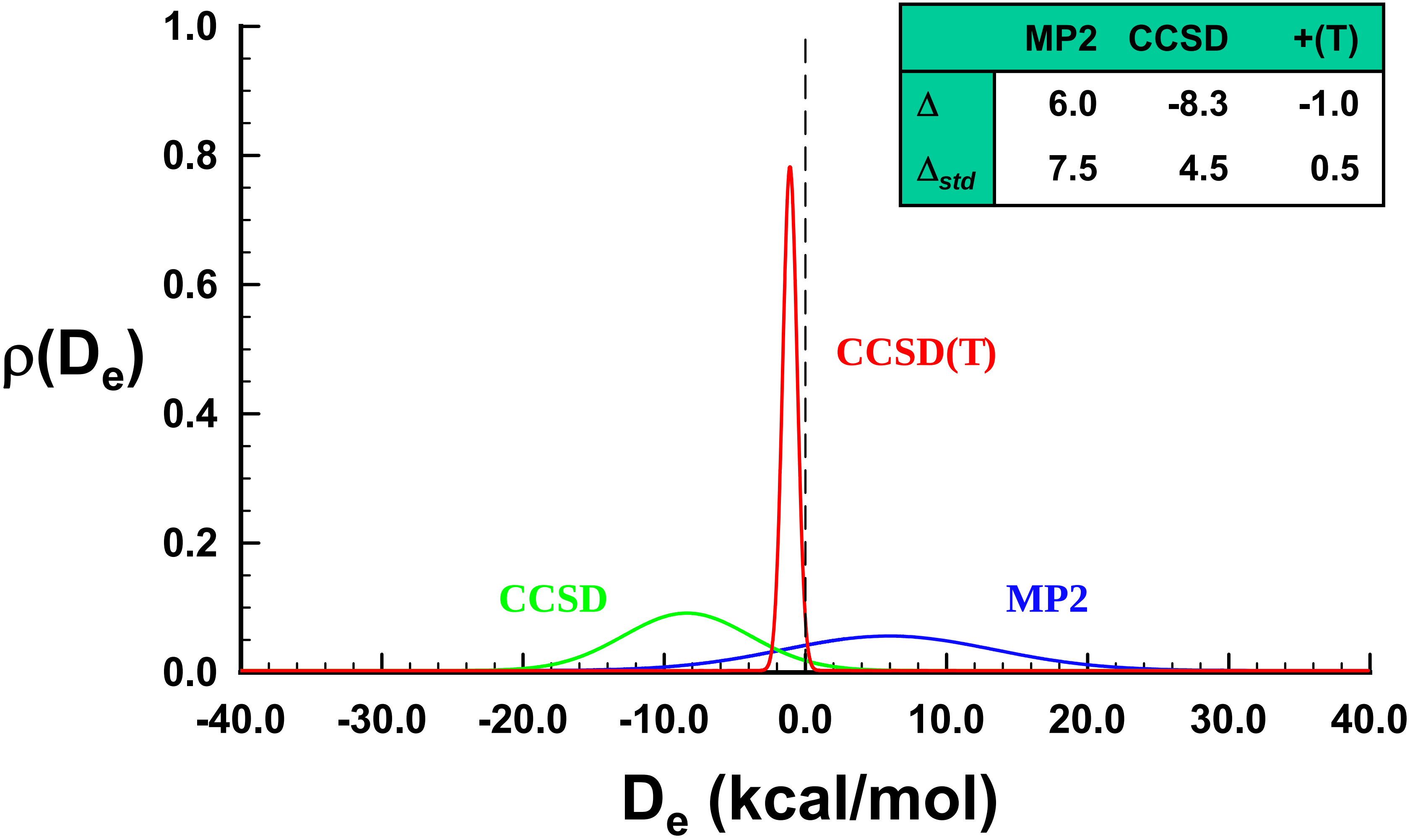
<EOM-CCSDT-3 <**EOM-CCSDT**<FULL CI

1996 2001

Performance of theories for the correlation energy in small molecules. To facilitate comparisons, the ordinate gives the size-scaling parameter of the approximation, $\alpha = \alpha_{\mathrm{n}} + \alpha_{\mathrm{N}} + \alpha_{\mathrm{it}}$ in the computational cost function $\mathrm{n}^{\alpha_{\mathrm{n}}}\mathrm{N}^{\alpha_{\mathrm{N}}}\mathrm{N}_{\mathrm{it}}^{\alpha_{\mathrm{it}}}$.

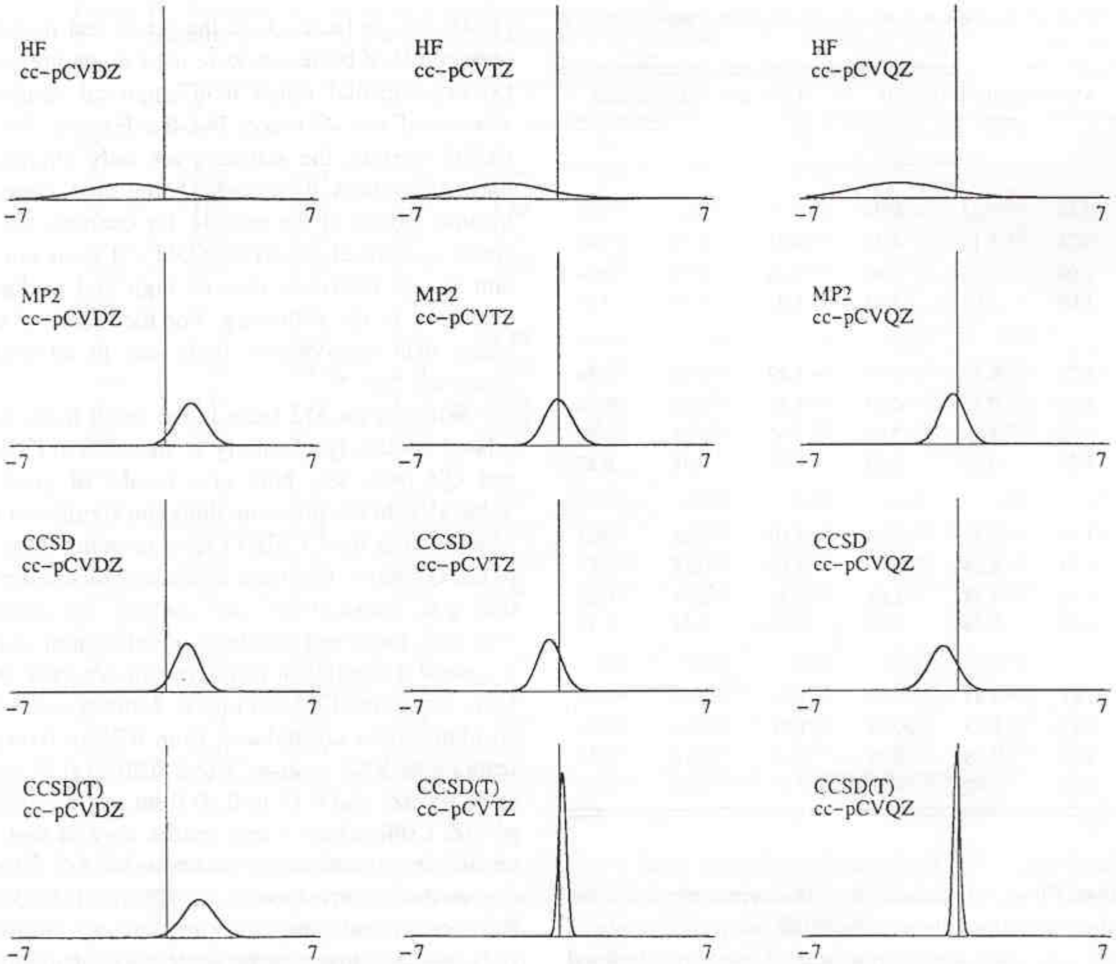


Coupled Cluster Calculation of D_e's



	MP2	CCSD	+(T)
Δ	6.0	-8.3	-1.0
Δ_{std}	7.5	4.5	0.5

From K. L. Bak et al., J. Chem. Phys. ***112****, 9229-9242 (2000)*



Normal distributions of errors in the calculated bond distances (pm). For ease of comparison, all distributions have been normalized to one and plotted against the same horizontal and vertical scales.

Bak, et. al., JCP (2001)

The alternative to such two-particle theories is an effective independent particle theory---

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

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

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

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

Correlated one-particle orbital theories have….

- Significant computational advantages

- Applicable to polymers and crystalline solids

- Conceptual advantages (frontier MO theory; energy bands)

- Might expect to get principal ionization potentials and electron affinities as eigenvalues (band gaps).

- Electronic spectra (excitons) should require two-particle effects, but zeroth-order (one-particle) spectra can be improved.

Kohn-Sham Density Functional Theory

$$E=E[\rho] = E_k + E_v[\rho] + E_J[\rho] + E_X[\rho] + E_C[\rho]$$

$$V_{XC}[\rho] = \delta E_{XC}[\rho] / \delta\rho$$

$$h_S \varphi_p = (t+v+J+V_{XC}) \varphi_p$$

$$\rho_{exact} = \Sigma\, \varphi_i(1)\varphi^*_i(1')$$

$\rho_{exact} - \rho_{KS} = 0$ **Defines a unique V_{XC}**

This density condition if the foundation for *ab initio dft*

Primary objective of our work in *ab initio dft* is to take the best of both worlds, WFT and DFT, and try to mold them into one superior method for applications to molecules. DFT does some things well, and WFT does others.

The conceptual model is coupled-cluster theory and its EOM-CC extensions for excited, ionized, electron-attached states, etc. Such two-electron methods coupled to converging basis sets have to converge to the exact solutions of the Schrodinger (Dirac) equation.

So we have to turn a two-particle theory into a one-particle one, with its potential computational and conceptual advantages, while retaining the rigor and convergence to the exact answer of the two-particle theory? One way is *ab initio dft.*

The critical quantity is the exchange-correlation potential.

OUTLINE

- *Ab initio dft*: What is it?
- How do we rigorously define Vxc?
- Form of the exact local exchange potential compared to PBE.
- Derivation of Vc, especially the right choice of unperturbed Ho.
- Comparisons of Vc from *ab initio dft* to that from PBE.
- Numerical consequences of *ab initio dft* Vxc compared to standard DFT & WFT.
- Dispersion interactions.
- Proof of a Koopmans'-like theorem for the eigenvalues in *ab initio dft* . Numerical results.
- Infinite-order generalizations (LCCSD) of MBPT2 functional for potentials.
- Potentials for open-shells and numerical consequences.
- Combination of non-local exchange with Vc.
- Time dependent *ab initio dft* .
- Conclusions

What is attractive about DFT?

- All results derive from an observable, the density.
- It is a one-particle theory that includes electron correlation.
    - *Applicable to larger molecules and solids
    - *Less basis set dependent
- It offers an attractive, conceptual foundation for chemistry.
- Excited states and other properties derive from a one-particle, TDDFT theory.
- Even poor potentials can often provide relatively good densities and associated energies. A case in point are the very successful ‘tack-on’-functionals for correlation.

(Oliphant, RJB, comparison to CCSD(T), JCP, 1995)

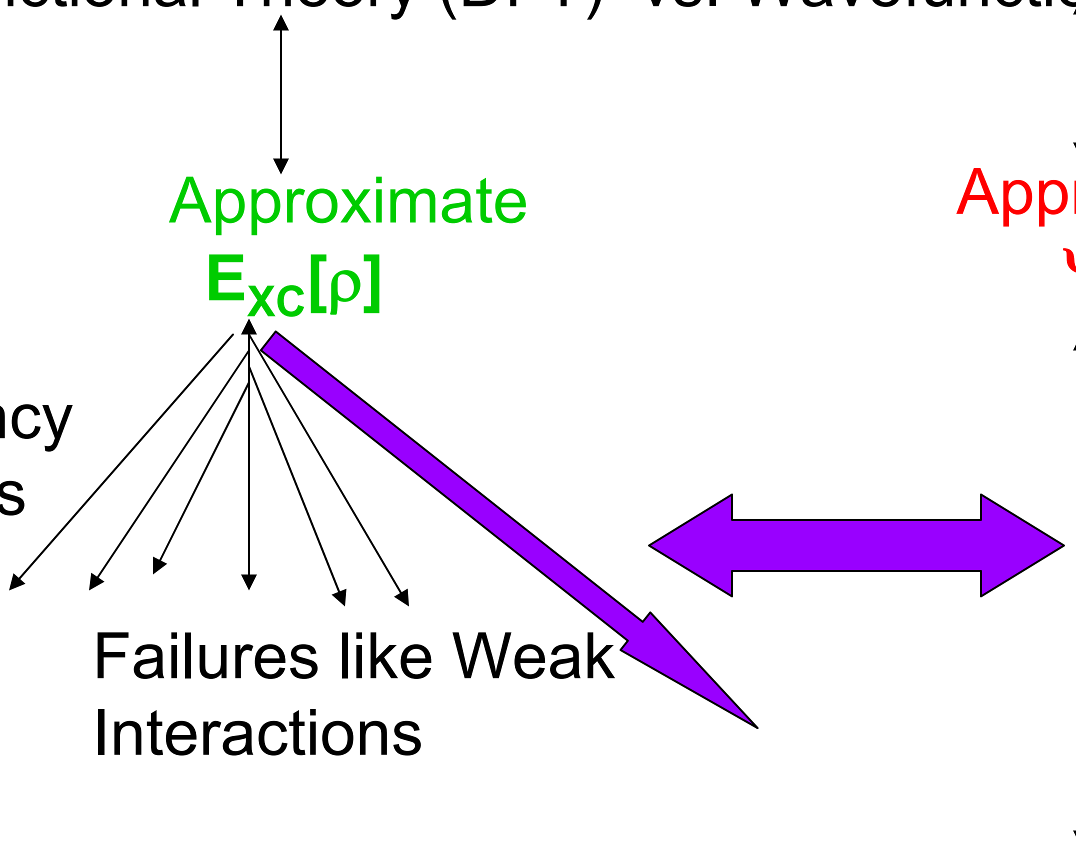
What is unattractive about DFT approximations?

•No guaranteed convergence to the right answer.
•No solution of the self-interaction problem.

Causes problems for---
*Anions,
* Photoelectron spectra,
* Rydberg excited states,
* Multiplets,
*Activation barriers.

•No proper inclusion of weak interactions.
All the above depend much more critically on the V_{XC} potential, and associated orbital dependent functionals.

Density Functional Theory (DFT) vs. Wavefunction Theory (WFT)



Approximate

$E_{xc}[\rho]$

Approximate

Ψ

Consistency Conditions

Failures like Weak Interactions

Basis Set and Correlation Limit

Exact Soln.

So what's the problem?

No one knows what $E[\rho]$ is.

True, but we do know that $E[\rho] = E[\rho(\varphi_i)]$, and that orbital dependent form is readily given by Coupled-Cluster theory and its MBPT approximations.

So we use those.

AB INITIO DFT

$$E=E_T + E_{ext} + E_H + E_X + E_{corr}$$

$$E=2\sum_I \langle I|h|I\rangle + \sum_{I,J}[2\langle IJ|IJ\rangle-\langle IJ|JI\rangle]$$

$+ \sum_{I<J,A<B} (2\langle IJ|AB\rangle - \langle IJ|BA\rangle)\langle IJ|AB\rangle/(\epsilon_I - \epsilon_J + \epsilon_A + \epsilon_B) + 2\sum_I |\langle I|f|A\rangle|^2/(\epsilon_I - \epsilon_A)$ +…(Notice we have a one- and a two-particle contribution to MBPT(2)+…)

OUR DEFINITION OF *AB INITIO DFT*

- Energy functional is given by orbital dependent expressions that are known to be exact through some order (or infinite order) in perturbation theory. (Implicit dft) WFT

- Potentials are derived from insisting that the exchange-correlation corrections to the density vanish (the KS condition) DFT

- Convergence to the exact answer in the limit of correlation corrections and basis set is guaranteed, like *ab initio* wavefunction methods. WFT

- Potentials (V_{XC}) are local and multiplicative, as required by dft. DFT

- Potentials are expressed in a basis set of (Gaussian) functions just as in *ab initio* wavefunction methods. There is no numerical integration. WFT

- To make the method practical, it is essential to use elements of GMBPT (RJB, Review, Modern Electronic Structure, Ed. D. Yarkony, 1995), WFT

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

- 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.
- There is no integer discontinuity problem.
- DFT unoccupied orbital energies (ϵ_a) enable a reasonable zeroth-order approximation for excitation energies to be ($\epsilon_a - \epsilon_i$), as in naïve Hueckel theory.
- 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.

At convergence, the KS density has to be exact.

In coupled-cluster theory we write it as

$$\rho(1) = \langle 0|(1+\Lambda)\exp(-T)\ \delta(x-x_1)\exp(T)|\ 0\rangle$$

$$= \langle 0|\exp(T^\dagger)\ \delta(x-x_1)\exp(T)|0\rangle$$

$= \rho_{KS} + \Delta\ \rho(1)$ and impose the condition

$\Delta\ \rho(1) = \sum \varphi_p(1)\gamma_{pq}\varphi_q(1) = 0$, to define $V_{XC.}$

This avoids any functional differentiation and is the only unambiguous way to employ superior separations to the Hamiltonian other than the standard KS choice, which is equivalent to functional differentiation

- To make the connection between WFT and DFT V_{XC} is defined by imposing the condition that the KS single determinant, Φ_{KS} , gives the exact ρ.

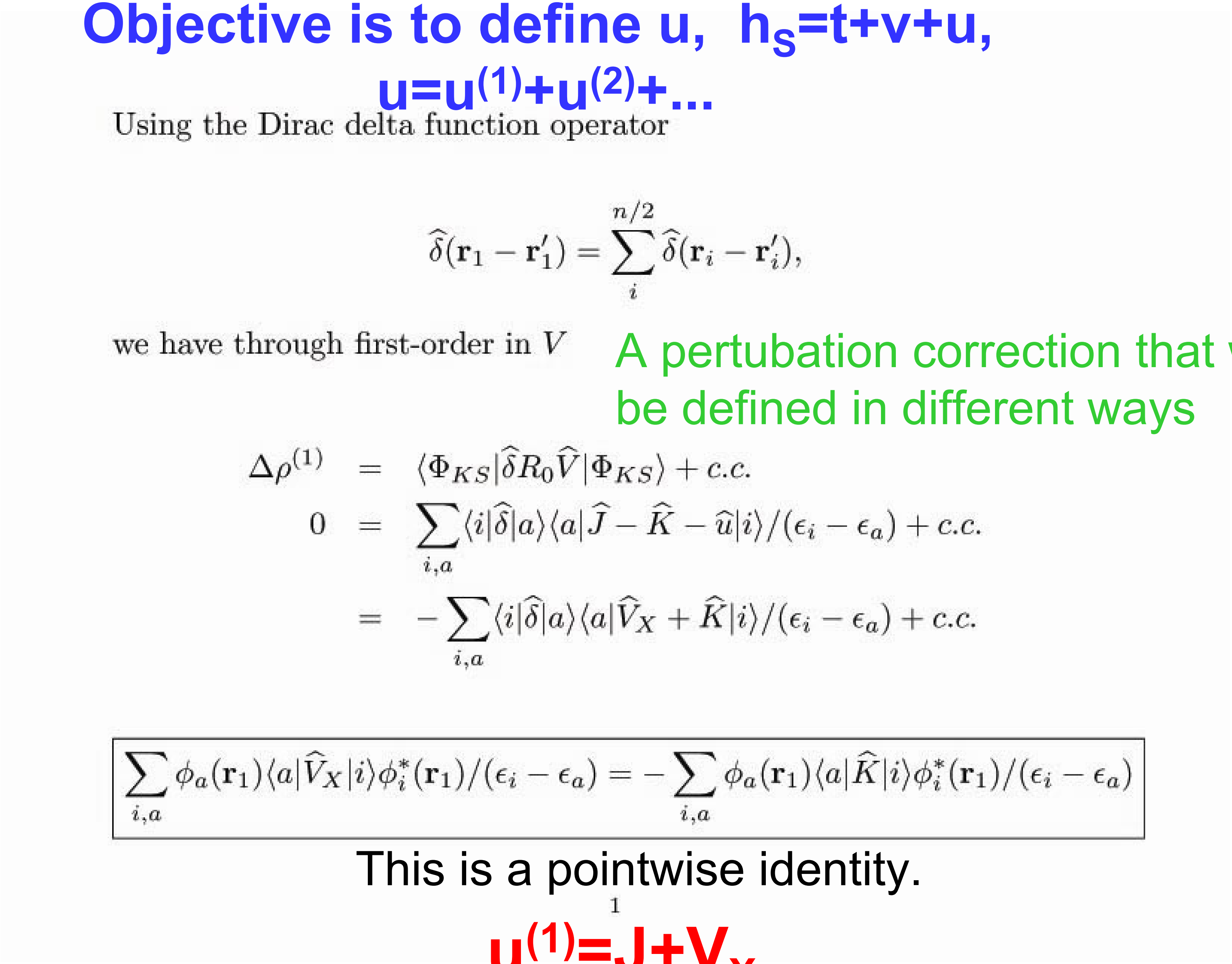
This is analogous to other choices for a single determinant…

- The HF determinant, $\Phi_{HF,}$ gives the lowest SD energy

- The first natural determinant, Φ_{N} , gives the best SD approximation to the density matrix

- The Brueckner determinant, Φ_{B} , gives the best possible SD overlap with the exact wavefunction

Objective is to define u, $h_S=t+v+u$, $u=u^{(1)}+u^{(2)}+\ldots$



Using the Dirac delta function operator

$$\widehat{\delta}(\mathbf{r}_1-\mathbf{r}_1') = \sum_i^{n/2} \widehat{\delta}(\mathbf{r}_i-\mathbf{r}_i'),$$

we have through first-order in V

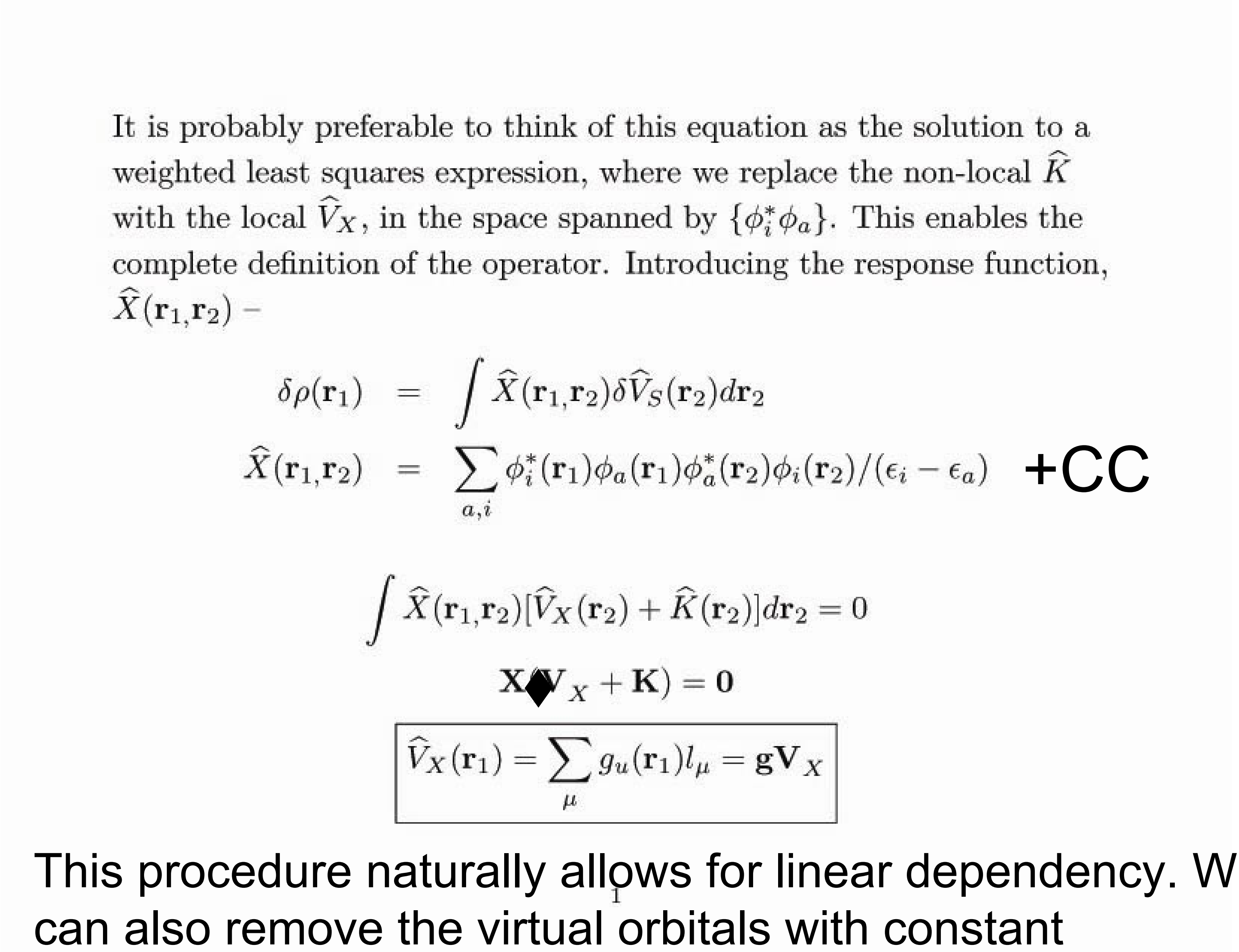
A pertubation correction that will be defined in different ways

$$\begin{aligned}
\Delta\rho^{(1)} &= \langle\Phi_{KS}|\widehat{\delta}R_0\widehat{V}|\Phi_{KS}\rangle + c.c. \\
0 &= \sum_{i,a}\langle i|\widehat{\delta}|a\rangle\langle a|\widehat{J}-\widehat{K}-\widehat{u}|i\rangle/(\epsilon_i-\epsilon_a) + c.c. \\
&= -\sum_{i,a}\langle i|\widehat{\delta}|a\rangle\langle a|\widehat{V}_X+\widehat{K}|i\rangle/(\epsilon_i-\epsilon_a) + c.c.
\end{aligned}$$

$$\boxed{\sum_{i,a}\phi_a(\mathbf{r}_1)\langle a|\widehat{V}_X|i\rangle\phi_i^*(\mathbf{r}_1)/(\epsilon_i-\epsilon_a) = -\sum_{i,a}\phi_a(\mathbf{r}_1)\langle a|\widehat{K}|i\rangle\phi_i^*(\mathbf{r}_1)/(\epsilon_i-\epsilon_a)}$$

This is a pointwise identity.

$$u^{(1)}=J+V_X$$



It is probably preferable to think of this equation as the solution to a weighted least squares expression, where we replace the non-local $\widehat{K}$ with the local $\widehat{V}_X$, in the space spanned by $\{\phi_i^*\phi_a\}$. This enables the complete definition of the operator. Introducing the response function, $\widehat{X}(\mathbf{r}_{1,}\mathbf{r}_2)$ –

$$\begin{aligned} \delta\rho(\mathbf{r}_1) &= \int \widehat{X}(\mathbf{r}_{1,}\mathbf{r}_2)\delta\widehat{V}_S(\mathbf{r}_2)d\mathbf{r}_2 \\ \widehat{X}(\mathbf{r}_{1,}\mathbf{r}_2) &= \sum_{a,i} \phi_i^*(\mathbf{r}_1)\phi_a(\mathbf{r}_1)\phi_a^*(\mathbf{r}_2)\phi_i(\mathbf{r}_2)/(\epsilon_i - \epsilon_a) \quad +\mathrm{CC} \end{aligned}$$

$$\int \widehat{X}(\mathbf{r}_{1,}\mathbf{r}_2)[\widehat{V}_X(\mathbf{r}_2) + \widehat{K}(\mathbf{r}_2)]d\mathbf{r}_2 = 0$$

$$\mathbf{X}(\blacklozenge\mathbf{V}_X + \mathbf{K}) = \mathbf{0}$$

$$\boxed{\widehat{V}_X(\mathbf{r}_1) = \sum_{\mu} g_u(\mathbf{r}_1)l_\mu = \mathbf{g}\mathbf{V}_X}$$

This procedure naturally allows for linear dependency. We can also remove the virtual orbitals with constant energy denominator and a closure condition.

Optimized effective potential (OEP)

finds a local effective potential whose corresponding self-consistent orbitals minimize the Hartree–Fock energy expression.

History

Slater (1951)——the localized HF exchange potential

Sharp & Horton (1953)——the idea & equation

Talman & Shadwick (1976)——the first atom calculations

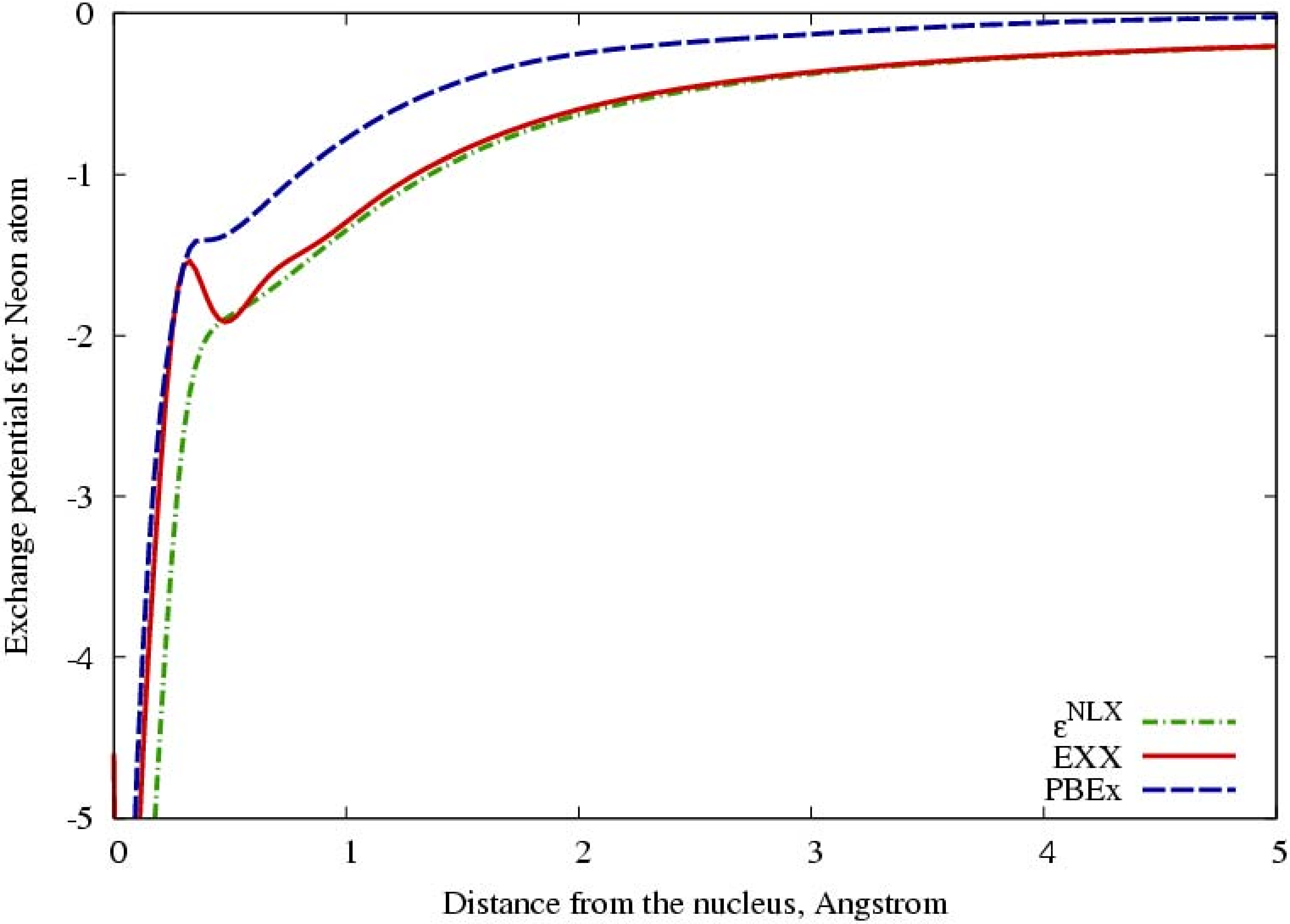
Krieger, Li, & Iafrate (1990)——the KLI approximation to OEP and numerical results

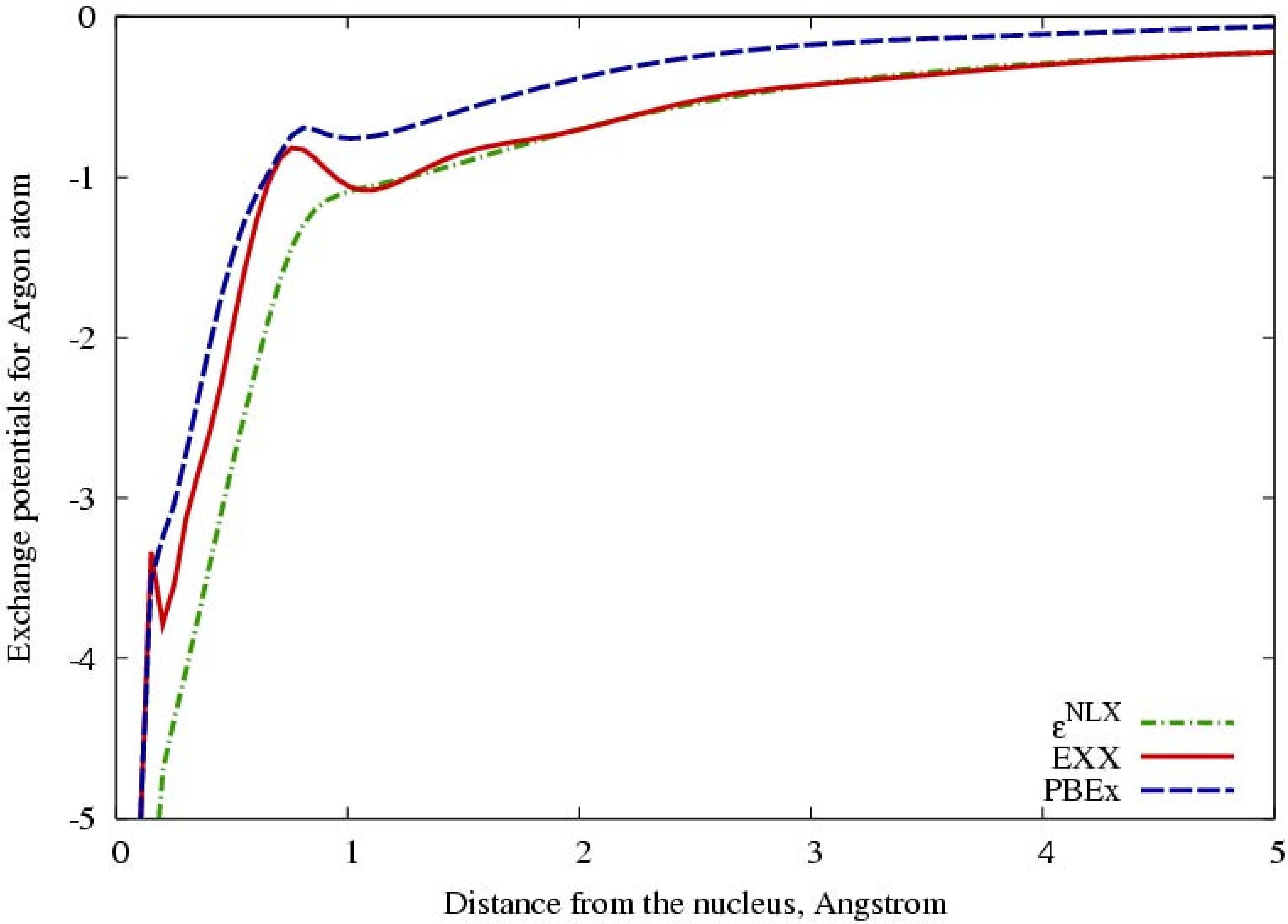
Kotani (1994)——the first crystalline solid calculations

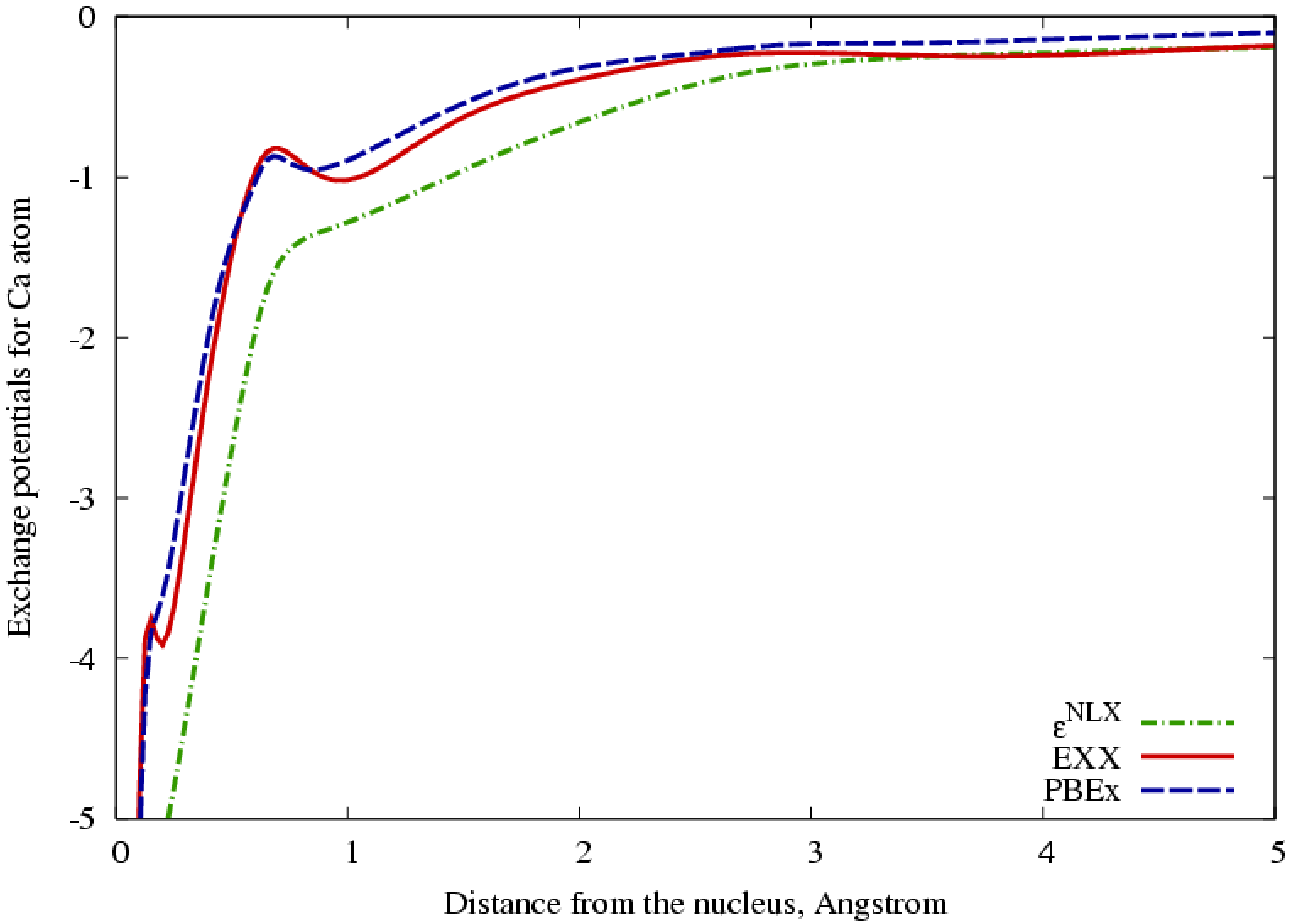
Ivanov, Hirata, & Bartlett (PRL,1999), first finite basis (Gaussian) implementation, EXX (Also known as OEP1 from its origin in the first-order density condition.)

Görling (1999), different realization of same (EXX) method

Gritsenko and Baerends (2001), CEDA approximation


Exchange potentials for Neon atom
Distance from the nucleus, Angstrom
0
-1
-2
-3
-4
-5
0
1
2
3
4
5
ε^{NLX}
EXX
PBEx


Exchange potentials for Argon atom
Distance from the nucleus, Angstrom
0
-1
-2
-3
-4
-5
0
1
2
3
4
5
ε^{NLX}
EXX
PBEx


Exchange potentials for Ca atom
0
-1
-2
-3
-4
-5
0
1
2
3
4
5
Distance from the nucleus, Angstrom
ε^{NLX}
EXX
PBEx

SECOND...

LET’S CONSIDER EXACT CORRELATION...

A LITTLE HISTORY OF ‘MANY-BODY THEORY’ INSPIRED CORRELATION POTENTIALS...

Sham-Schlüter, PRL 1983. Constant density propagator approach. Formal.

Görling-Levy, PRA, IJQC 1993-1996. RSPT at constant density, subject to KS unperturbed problem. Formal.

Engel,Dreizler, Bonetti, PRL 1998-2001. Numerical calculations with only doubles part of MBPT(2), not self-consistent.

Grabowski, Hirata, Ivanov, RJB, JCP, 2002. First full, self-consistent, MBPT(2) *ab initio dft* results, subject to KS unperturbed problem.

RJB, Grabowski, Hirata, Ivanov, JCP, 2004. Transition from KS hamiltonian, which usually causes divergence, to well-behaved GMBPT.

RJB, Lotrich, Schweigert 2005-Special JCP Issue on DFT. Theory and extensive numerical results of *ab initio dft.*

RJB, Schweigert, Lotrich 2006-Proceedings WATOC, Theochem. Other theory and results of *ab initio dft.*

Bokhan, RJB, 2006, Chem Phys. Letters, Open shells.

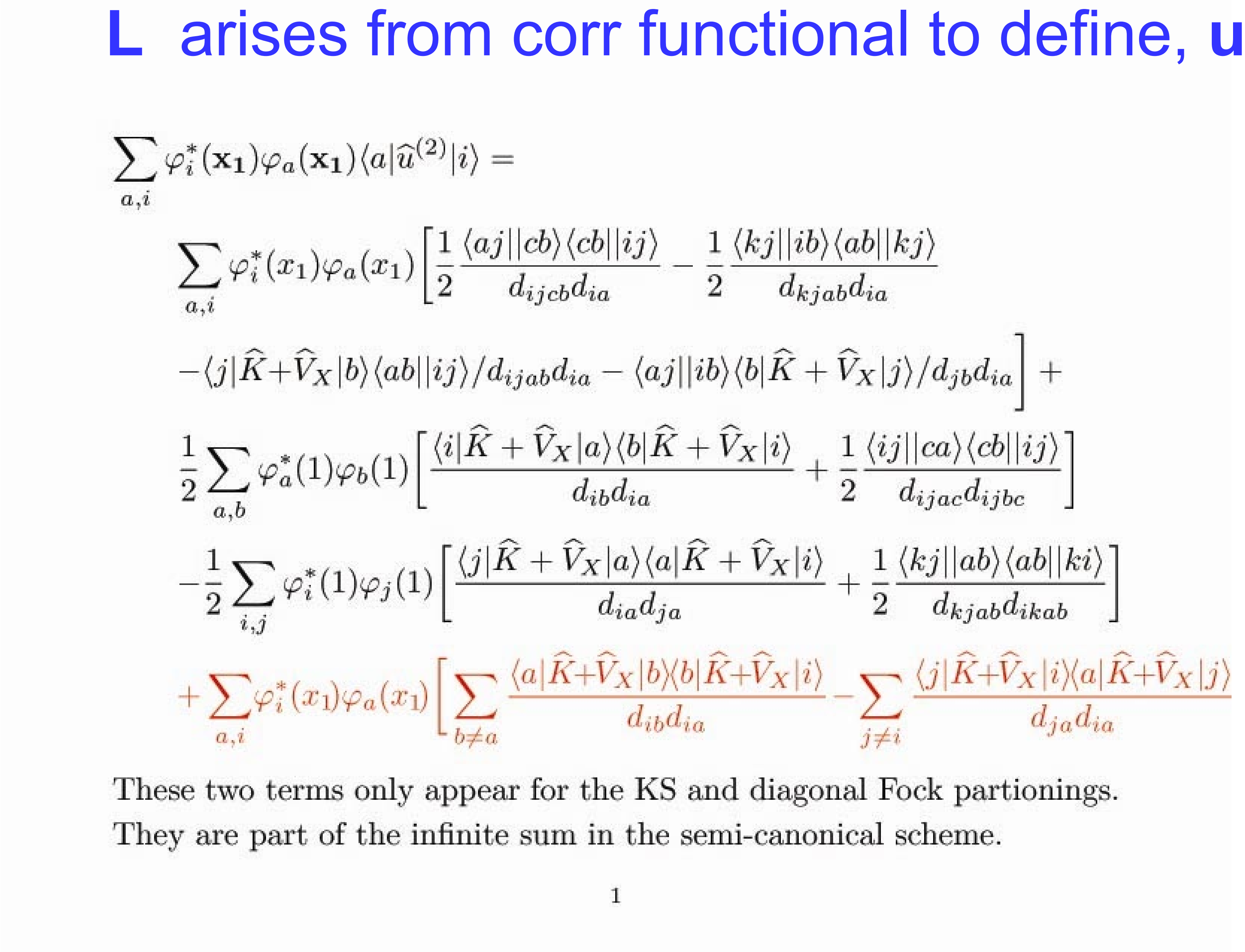
In the next (second) order, we have

$$\Delta\rho^{(2)} = \langle\Phi_{KS}|\widehat{\delta}R_0\widehat{V}R_0\widehat{V}|\Phi_{KS}\rangle+\langle\Phi_{KS}|\widehat{V}R_0\widehat{\delta}R_0\widehat{V}|\Phi_{KS}\rangle+\langle\Phi_{KS}|\widehat{V}R_0\widehat{V}R_0\widehat{\delta}|\Phi_{KS}\rangle$$

$$\mathbf{X}\blacklozenge\mathbf{V}_{XC}+\mathbf{K}+\mathbf{L})=\mathbf{0}$$

Defines a local, second-order correlation potential to augment V_X,

L arises from corr functional to define, $\mathbf{u}^{(2)}$



$$\sum_{a,i}\varphi_i^*(\mathbf{x_1})\varphi_a(\mathbf{x_1})\langle a|\widehat{u}^{(2)}|i\rangle =$$

$$\sum_{a,i}\varphi_i^*(x_1)\varphi_a(x_1)\Big[\frac{1}{2}\frac{\langle aj||cb\rangle\langle cb||ij\rangle}{d_{ijcb}d_{ia}} - \frac{1}{2}\frac{\langle kj||ib\rangle\langle ab||kj\rangle}{d_{kjab}d_{ia}}$$

$$-\langle j|\widehat{K}+\widehat{V}_X|b\rangle\langle ab||ij\rangle/d_{ijab}d_{ia} - \langle aj||ib\rangle\langle b|\widehat{K}+\widehat{V}_X|j\rangle/d_{jb}d_{ia}\Big] +$$

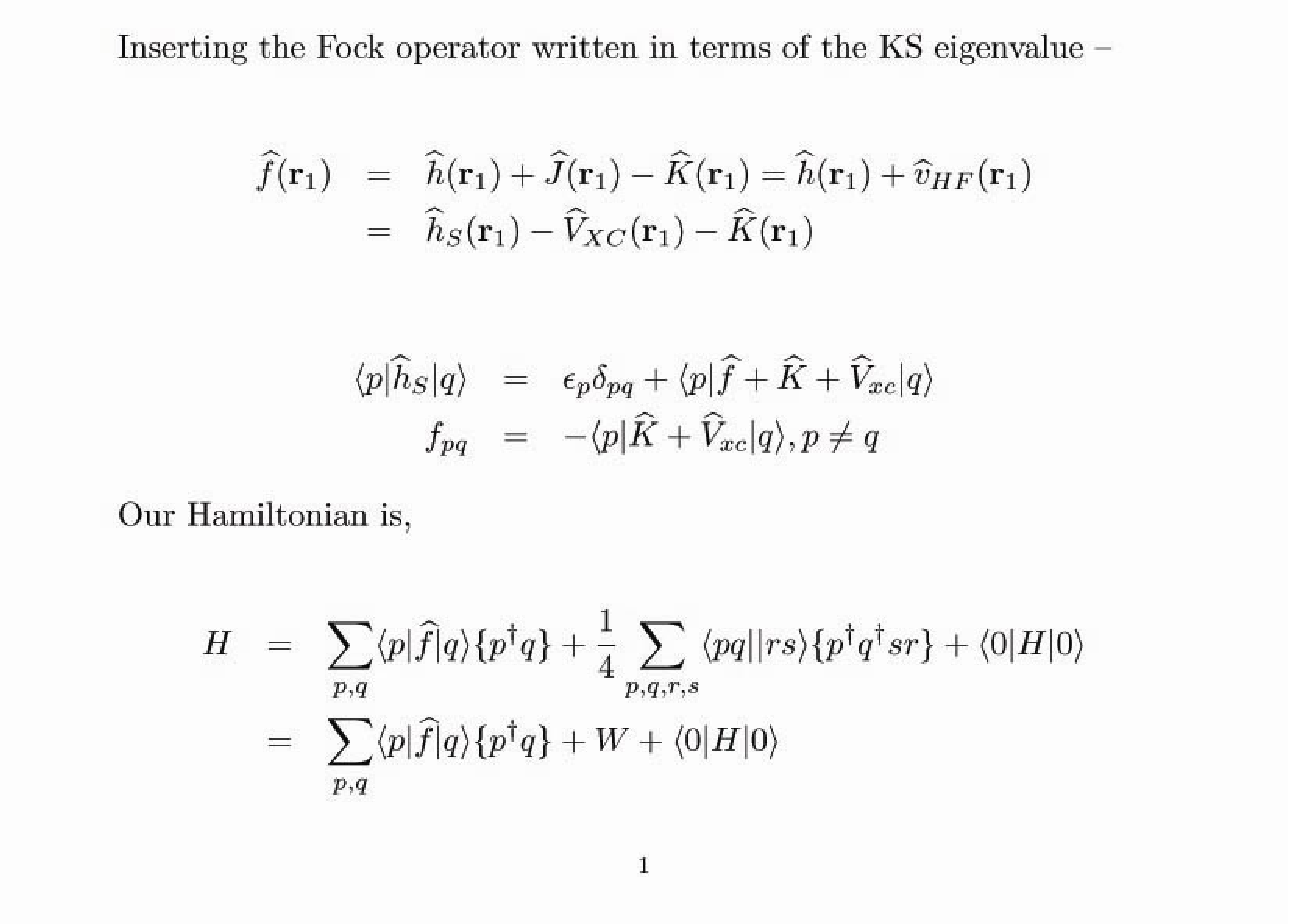
$$\frac{1}{2}\sum_{a,b}\varphi_a^*(1)\varphi_b(1)\Big[\frac{\langle i|\widehat{K}+\widehat{V}_X|a\rangle\langle b|\widehat{K}+\widehat{V}_X|i\rangle}{d_{ib}d_{ia}} + \frac{1}{2}\frac{\langle ij||ca\rangle\langle cb||ij\rangle}{d_{ijac}d_{ijbc}}\Big]$$

$$-\frac{1}{2}\sum_{i,j}\varphi_i^*(1)\varphi_j(1)\Big[\frac{\langle j|\widehat{K}+\widehat{V}_X|a\rangle\langle a|\widehat{K}+\widehat{V}_X|i\rangle}{d_{ia}d_{ja}} + \frac{1}{2}\frac{\langle kj||ab\rangle\langle ab||ki\rangle}{d_{kjab}d_{ikab}}\Big]$$

$$+\sum_{a,i}\varphi_i^*(x_1)\varphi_a(x_1)\Big[\sum_{b\neq a}\frac{\langle a|\widehat{K}+\widehat{V}_X|b\rangle\langle b|\widehat{K}+\widehat{V}_X|i\rangle}{d_{ib}d_{ia}} - \sum_{j\neq i}\frac{\langle j|\widehat{K}+\widehat{V}_X|i\rangle\langle a|\widehat{K}+\widehat{V}_X|j\rangle}{d_{ja}d_{ia}}$$

These two terms only appear for the KS and diagonal Fock partionings. They are part of the infinite sum in the semi-canonical scheme.

Origin of different partitionings...



Inserting the Fock operator written in terms of the KS eigenvalue –

$$
\begin{aligned}
\widehat{f}(\mathbf{r}_1) &= \widehat{h}(\mathbf{r}_1) + \widehat{J}(\mathbf{r}_1) - \widehat{K}(\mathbf{r}_1) = \widehat{h}(\mathbf{r}_1) + \widehat{v}_{HF}(\mathbf{r}_1) \\
&= \widehat{h}_S(\mathbf{r}_1) - \widehat{V}_{XC}(\mathbf{r}_1) - \widehat{K}(\mathbf{r}_1)
\end{aligned}
$$

$$
\begin{aligned}
\langle p|\widehat{h}_S|q\rangle &= \epsilon_p\delta_{pq} + \langle p|\widehat{f} + \widehat{K} + \widehat{V}_{xc}|q\rangle \\
f_{pq} &= -\langle p|\widehat{K} + \widehat{V}_{xc}|q\rangle, p \neq q
\end{aligned}
$$

Our Hamiltonian is,

$$
\begin{aligned}
H &= \sum_{p,q}\langle p|\widehat{f}|q\rangle\{p^\dagger q\} + \frac{1}{4}\sum_{p,q,r,s}\langle pq||rs\rangle\{p^\dagger q^\dagger sr\} + \langle 0|H|0\rangle \\
&= \sum_{p,q}\langle p|\widehat{f}|q\rangle\{p^\dagger q\} + W + \langle 0|H|0\rangle
\end{aligned}
$$

and the one-particle part becomes –

$$\begin{aligned}\sum_{p,q}\langle p|\widehat{f}|q\rangle\{p^{\dagger}q\} &= \sum_{p}[\epsilon_p-\langle p|\widehat{K}+\widehat{V}_{xc}|p\rangle]\{p^{\dagger}p\}-\sum_{p\neq q}\langle p|\widehat{K}+\widehat{V}_{xc}|q\rangle\{p^{\dagger}q\}\\ &= H_0(KS)-\sum_{p}\Delta_{pp}-\sum_{p\neq q}\Delta_{pq}=H_0(KS)-\Delta\end{aligned}$$

$$\boxed{V(KS)=W-\Delta}$$

where Δ distinguishes our approach from standard KS.

$$\mathbf{H=H_0(KS)+V(KS)}$$

Table 1. Total energies(au))

MAD (KJ/mol)	MP2 **58.2**	OEP2-ks **GLPT2**	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_2O	-76.370003	-76.510744	-76.373092	-76.369991	-76.383576
H_2O^+	-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

In the KS case Δ contains a diagonal term, Δ_{pp}, that is now part of the perturbation. This is likely to cause problems with convergence. This choice means that all denominators in the equations above are composed of KS eigenvalues.

Alternatively, if we make the diagonal f$_{pp}$ choice

$$H_0(df) = \sum_p \langle p|\widehat{f}|p\rangle \{p^\dagger p\}$$

$$\boxed{V(df) = W - \sum_{p \neq q} \Delta_{pq}}$$

We eliminate the diagonal term and our denominators $d_{ia} = (f_{ii} - f_{aa}) = (\epsilon_i - \epsilon_a) - (\langle i|K + V_{XC}|i\rangle - \langle a|K + V_{XC}|a\rangle)$.

$$H=H_0(df)+V(df)$$

This third, semi-canonical, choice also addresses part of the Δ_{pq} term,

$$\Delta_{pq} = f_{pq}\{p^\dagger q\} = f_{ij}\{i^\dagger j\} + f_{ab}\{a^\dagger b\} + f_{ai}\{a^\dagger i\} + f_{ia}\{i^\dagger a\}$$

by making a semi-canonical transformation that makes

$$\mathbf{f} = \begin{bmatrix} \diagdown & \blacksquare \\ \blacksquare & \diagdown \end{bmatrix}$$

Then, subject to these new orbtilas –

$$H_0 = \sum_{\tilde{p}} f_{\tilde{p}\tilde{p}} \tilde{p}^\dagger \tilde{p}$$

$$\boxed{V = \sum_{\tilde{a},\tilde{i}} f_{\tilde{a}\tilde{i}} \left(\tilde{a}^\dagger \tilde{i} + \tilde{i}^\dagger \tilde{a}\right) + \tilde{W}}$$

where all of $\sum_{i \neq j} \Delta_{ij}$ and $\sum_{a \neq b} \Delta_{ab}$ are now subsummed into H_0.

$H=H_0(sc)+V(sc)$

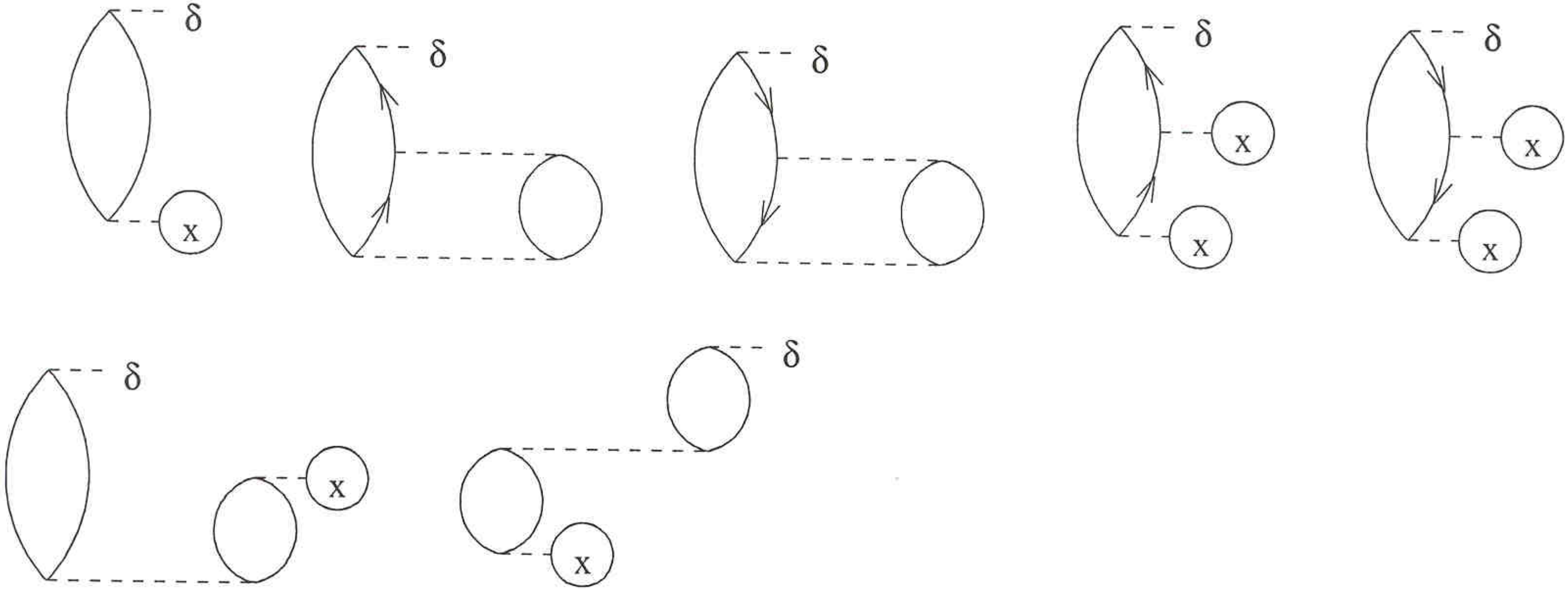
The partitionings...

- H_0 (SC) is invariant to any transformation of occupied or virtual orbitals.

- Diagonal contribution is included to all orders in even low orders of PT (Fdiag only uses this)

- Third (standard) approximation is to use KS denominators

Will use three approximations: KS denominators, Fdiag, SC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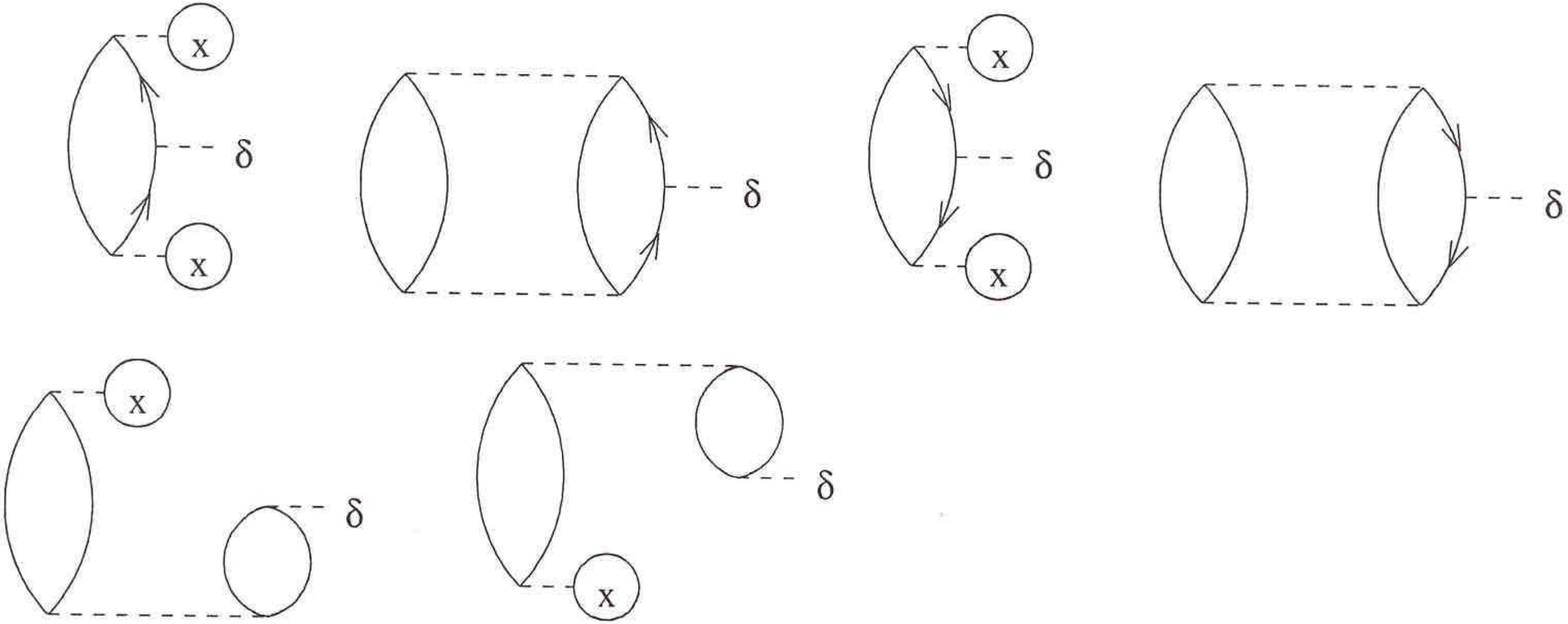
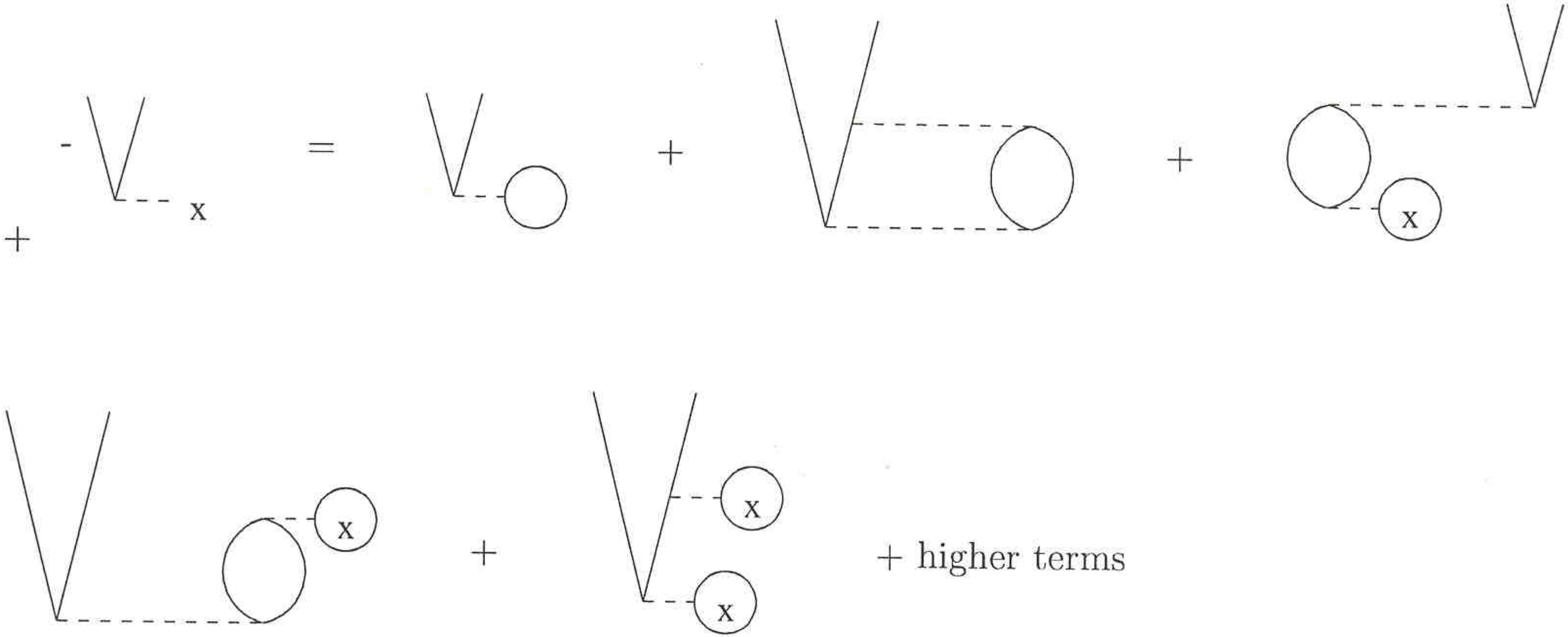

x
δ
x
δ
x
δ
x
δ
x
δ
δ
x

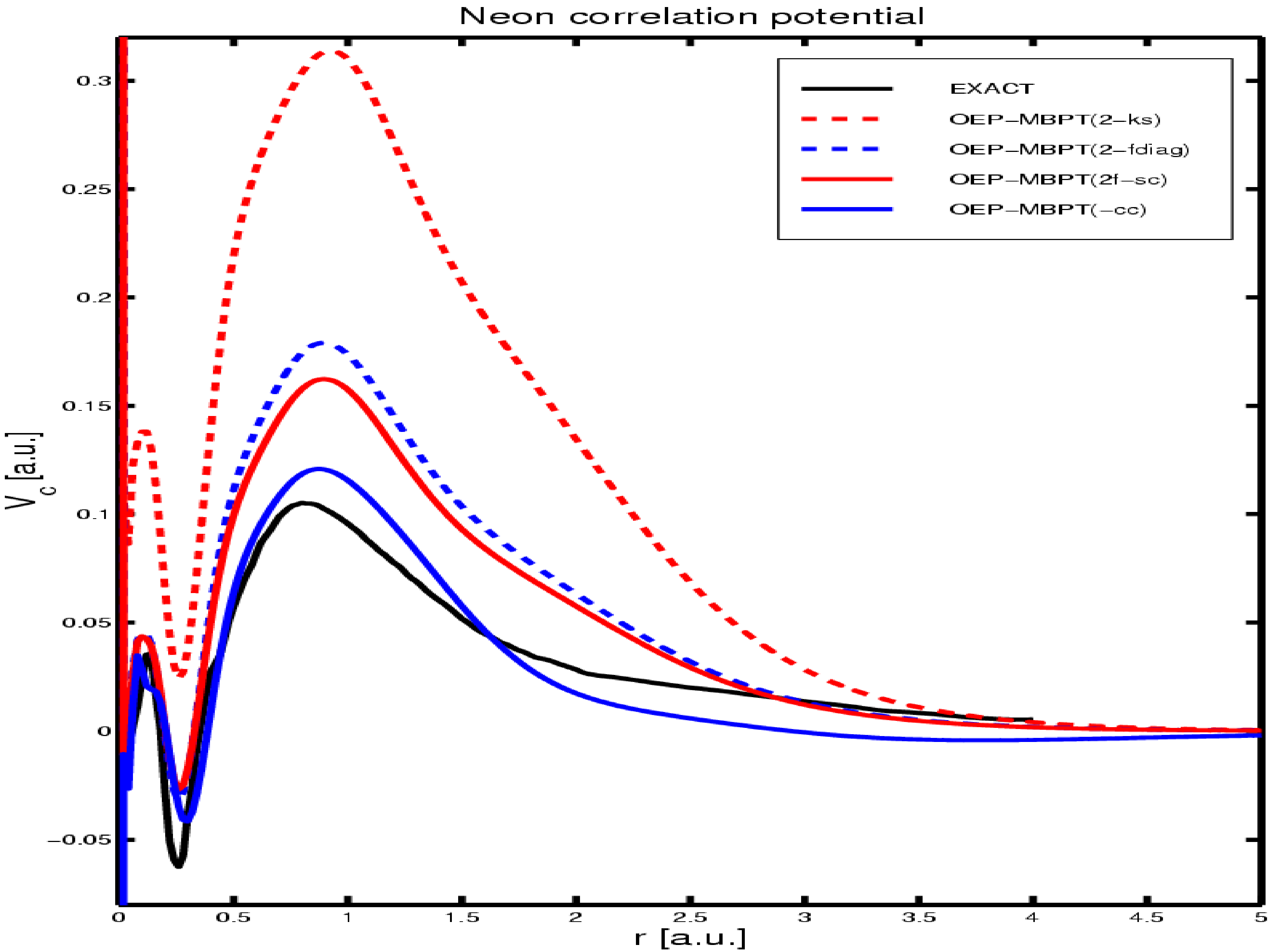

+
-
x
=
+
+
x
x
+
x
x
+ higher terms

What are the possible differences in a second order calculation?

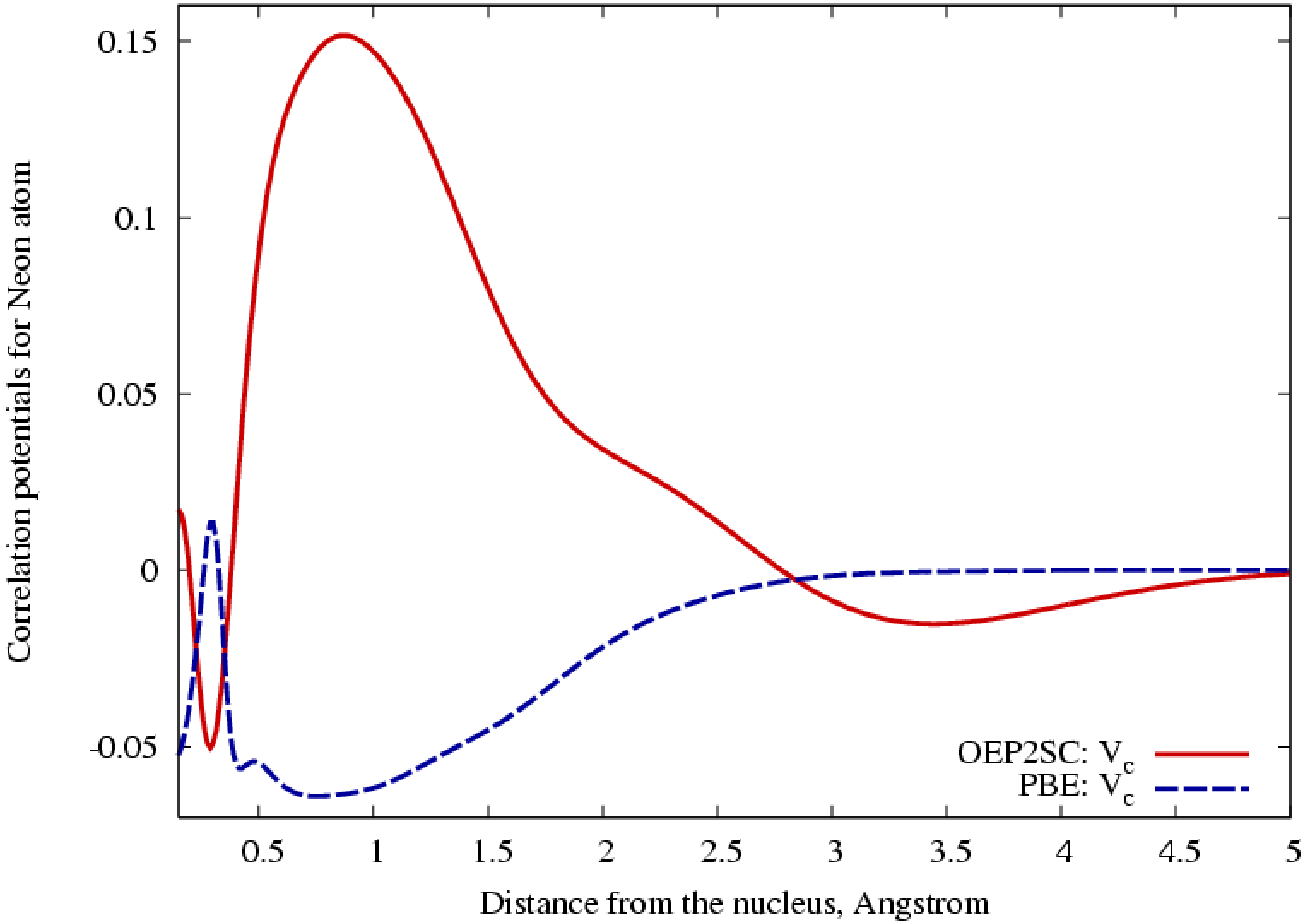
1. Functional differentiation vs. density condition?
2. Use of just doubles or singles and doubles in orbital dependent functionals?
3. Whether the determination of $V_C^{(2)}$ in an iteration depends only on V_X, or in general if $V_{XC}^{(n)}$ is determined by $V_{XC}^{(n-1)}$, $V_{XC}^{(n-2)}$, …That is, whether the potential to be determined appears on both sides of equation, or just one. Insistence on a specific order forces the latter..
4. Whether this is done with predetermined KS orbtals, or fully self-consistently. The latter makes the KS orbitals, functional, and density consistent to same order.
5. Whether $H_0=\Sigma\varepsilon_p^{(KS)}\{p^\dagger p\}$, the KS choice, or $H_0 =\Sigma f_{pp}\{p^\dagger p\} + f_{ij}\{i^\dagger j\} + f_{ab}\{a^\dagger b\}$, our semi-canoncial choice.

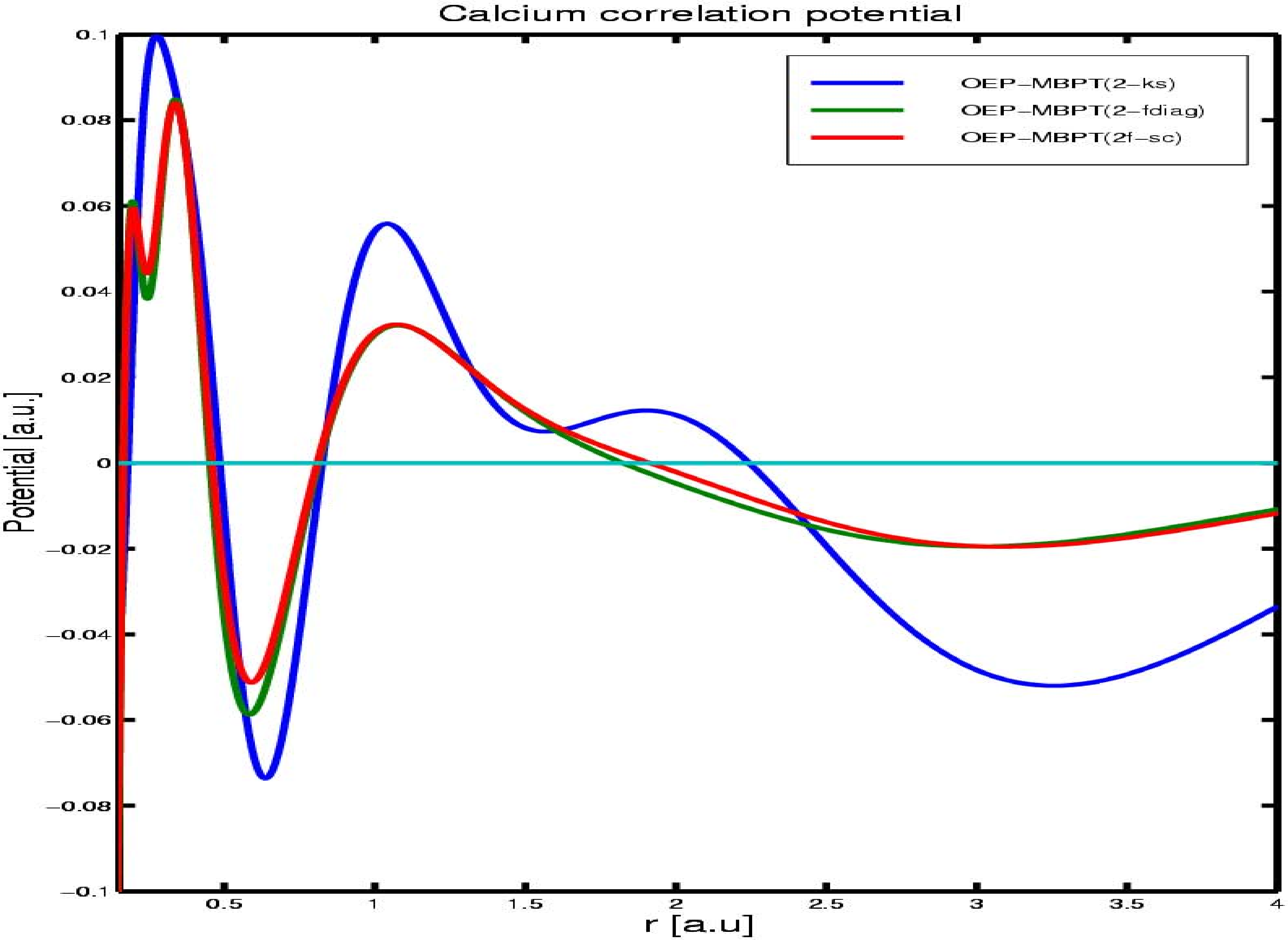
OUR CHOICES, AFTER FIRST PAPER, ARE THE BLUE ONES.

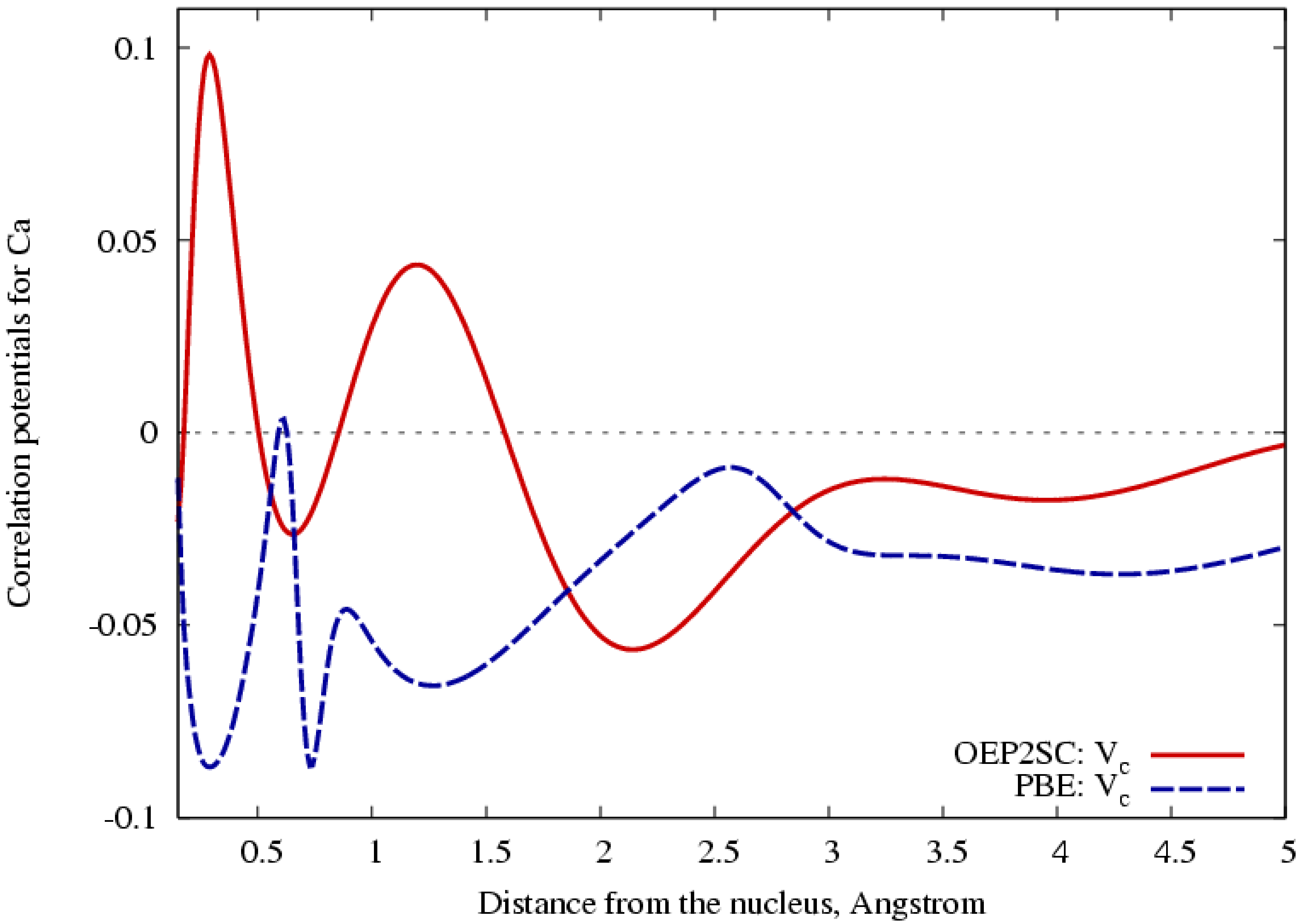
Goerling-Levy, Engel, and Mori-Sanchez... Yang made different choices, which greatly affects the convergence (and, indeed, even the possibility) for such a method.

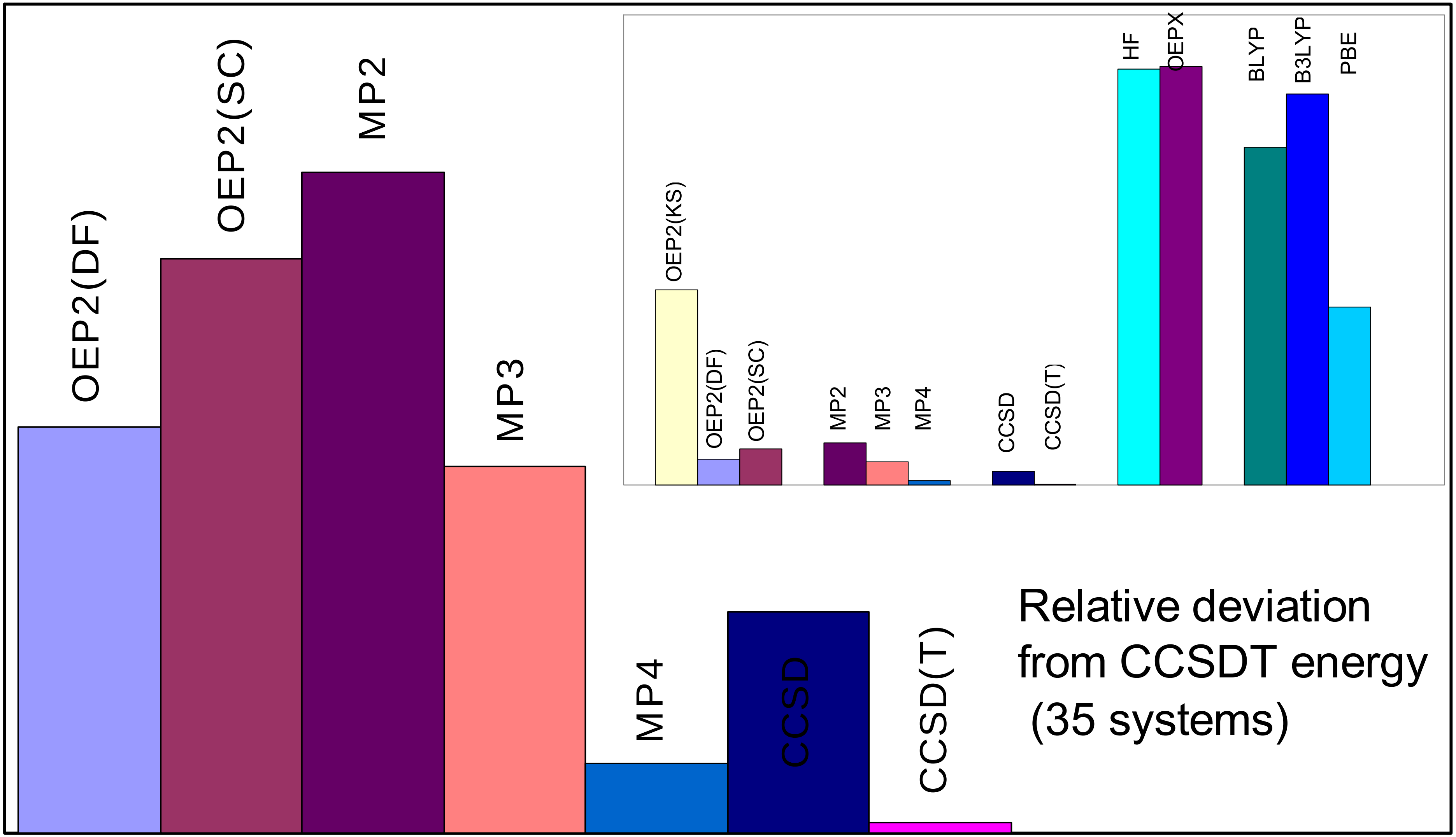


Exact QMC result from Umrigar, Gonze.

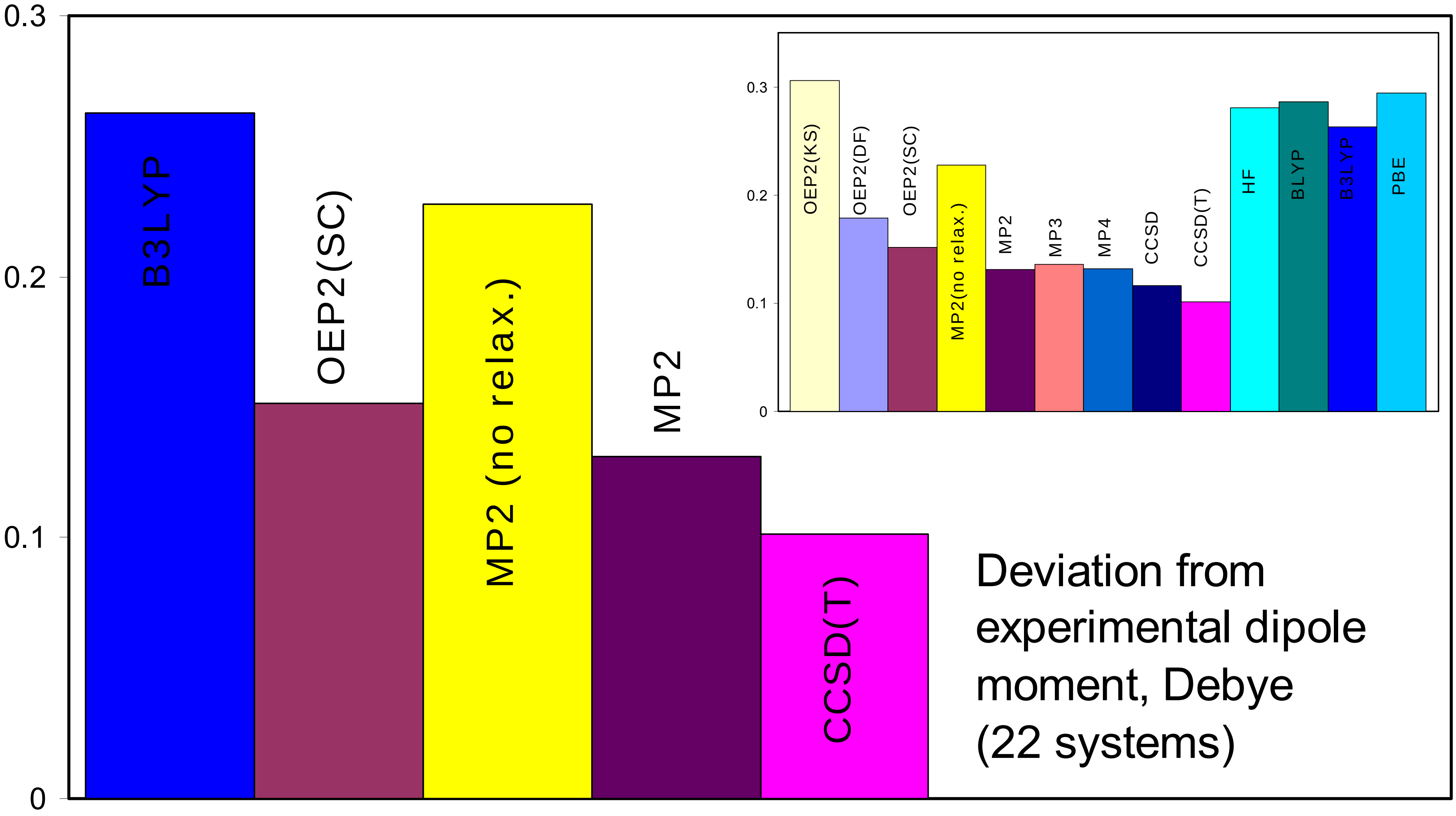

Correlation potentials for Neon atom
Distance from the nucleus, Angstrom
0.15
0.1
0.05
0
-0.05
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
OEP2SC: V_c
PBE: V_c


Calcium correlation potential
OEP–MBPT(2–ks)
OEP–MBPT(2–fdiag)
OEP–MBPT(2f–sc)
Potential [a.u.]
r [a.u]
0.1
0.08
0.06
0.04
0.02
0
–0.02
–0.04
–0.06
–0.08
–0.1
0.5
1
1.5
2
2.5
3
3.5
4

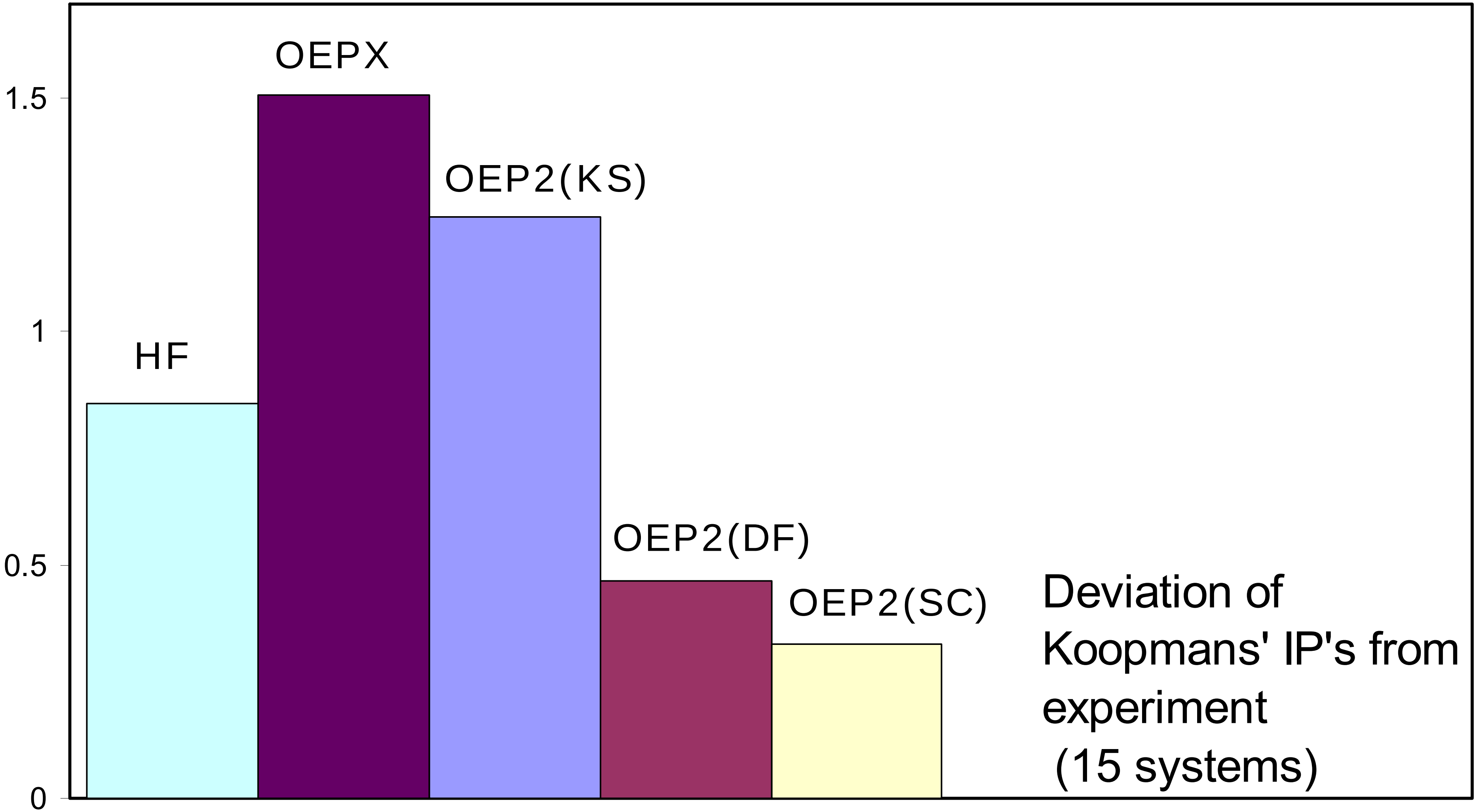

Correlation potentials for Ca
Distance from the nucleus, Angstrom
0.1
0.05
0
-0.05
-0.1
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
OEP2SC: V_c
PBE: V_c



Relative deviation
from CCSDT energy
(35 systems)



Deviation from experimental dipole moment, Debye (22 systems)



Deviation of Koopmans' IP's from experiment
(15 systems)

WHAT ABOUT ORBITAL ENERIGES AND EXCITATION ENERGIES IN *AB INITIO DFT*?

Using TDDFT in the adiabatic approximation, and simply making 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 the **A** and **B** matrices, the eigenvalues of the KS equations using realistic OEP based potentials should approximately correspond to ionization potentials.

This is a Koopmans' approximation for KS-DFT that ascribes meaning to the orbital energies.

RJB, VL, IS, JCP (2005), Special Issue

Comparison of OEP2(sc) Orbital Energies with IP-EOM-CC, OEPx, HF (eV)

Molecules: NH_3, CH_4, CO, N_2

	OEP2(sc)	OEPx	HF
Homo	0.4	0.9	0.8
Homo-1	0.5	0.8	0.9
Homo-2	0.8	0.8	2.6

THERE IS NOTHING KEEPING US FROM COMBINING THE LOCAL CORRELATION POTENTIAL WITH A HF SOLUTION, IE ONE THAT USES FULL NON-LOCAL EXCHANGE.

ADVANTAGES

- The homo condition (ie <h|Vx|h>=-<h|K|h> that is difficult for OEPx to satisfy in a basis is bypassed.
- Charge transfer is correctly described in zeroth order in HF, but not in DFT.
- Koopmans' theorem applies to the HF orbita lenergies.

DISADVANTAGES

- OEP-DFT orbitals provide a good zeroth-order excitation spectrum.
- Potential advantages due to the cancellation between exchange and correlation do not apply

Principal ionization potentials (eV) of the water molecule estimated from the occupied orbital energies. The first row gives experimental values (eV) and the subsequent rows give the deviation from the experimental values for various methods. IP-EOM-CCSD values are shown for comparison.

IP	Expt.	HF	HF/ PT2	EXX	EXX/ PT2SC	HF+EXX	HF+EXX/ PT2	HF+EXX/ PT2SC	IP-EOM-CCSD
b1	12.62	+1.23	-0.63	+1.82	**-0.10**	+1.52	-1.37	**-0.36**	-0.11
a1	14.74	+1.16	-0.44	+1.61	**-0.15**	+1.37	-1.23	**-0.29**	0.00
b2	18.51	+1.10	-0.21	+1.45	**-0.06**	+1.28	-0.97	**-0.13**	+0.52
a1	32.61	+4.21	+2.44	0.00	**-1.91**	+2.10	-0.72	**+0.27**	+0.06
a1	539.7	+19.9	+20.8	-23.0	**-22.4**	-1.6	-0.7	**-0.8**	+1.7

Principal ionization potentials (eV) of the carbon monoxide molecule estimated from the occupied orbital energies. The first row gives IP-EOM-CCSD values (eV) and the subsequent rows give the difference (eV) between these values and orbital energies for various methods. Uncontracted double-zeta set of atomic natural orbitals (P.O. Widmark, P.A. Malmqvist, B.O. Roos, Theor. Chim. Acta **77**, 1990) was used as both atomic and potential basis sets.

IP-EOM-CCSD	HF	EXX	EXX-PT2SC	HF+EXX+PT2SC
14.17	0.95	0.84	**-0.64**	**0.48**
17.02	0.39	0.87	**-0.88**	**-0.07**
19.77	2.16	0.87	**-1.24**	**0.50**
37.26	4.20	-0.98	**-3.55**	**0.09**
297.53	11.63	-18.68	**-18.91**	**-2.61**
544.22	18.13	-25.40	**-24.73**	**-1.77**

Energy and dipole moment

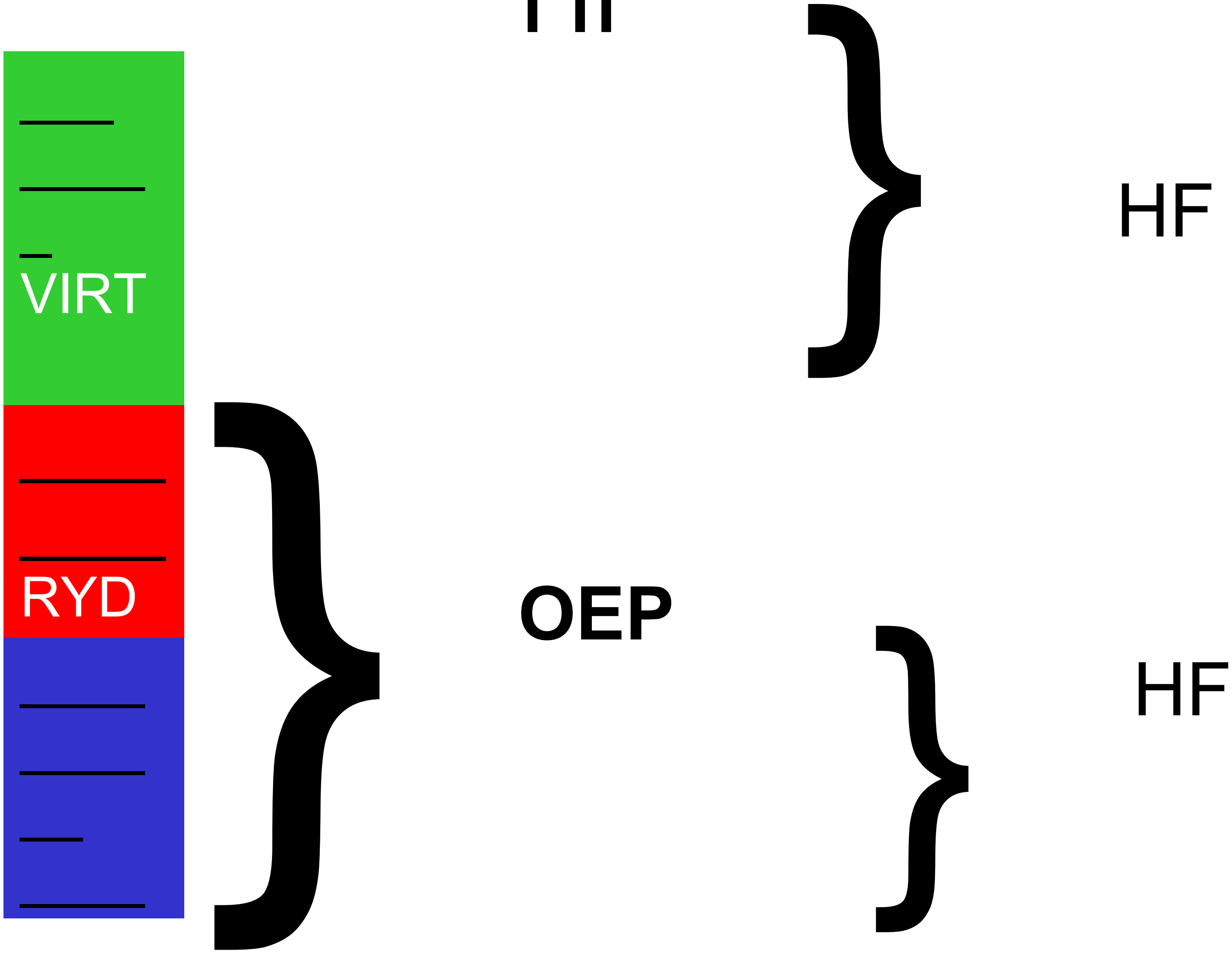
Method	Energy[a]	Dipole[b]
HF	0.234	0.28
OEP2(KS)	0.104	0.31
OEP2(SC)	0.019	0.15
OEP2(NLX)	0.018	0.19
MBPT(2)	0.022	0.23 (0.13[c])
MBPT(4)	0.002	0.13[c]
CCSD	0.007	0.11

[a] Average relative deviation from CCSDT (35 systems)

[b] Average absolute deviation from experiment, Debye (22 syster

[c] With orbital relaxation effects included

Orbital energies in OEP and HF



HF

VIRT

RYD

OEP

HF

Estimated Excitation Energies from OEP2(sc) and OEPx Orbital Energies ($\epsilon_a - \epsilon_i$) compared to EOM-CC

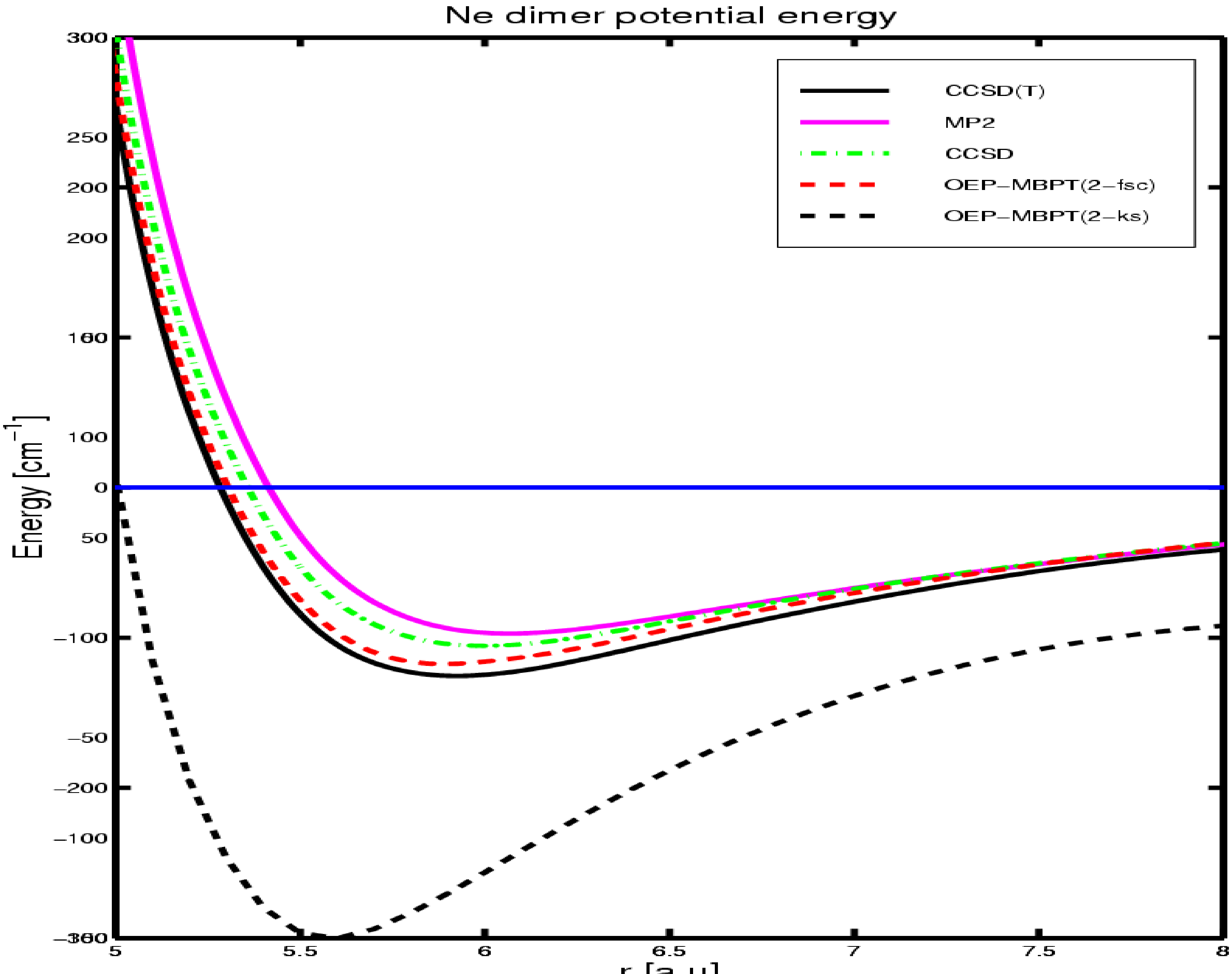
MOLECULES: H_2O(Rydberg), N_2 (valence)

OEP2 (sc) MAE=0.66 eV

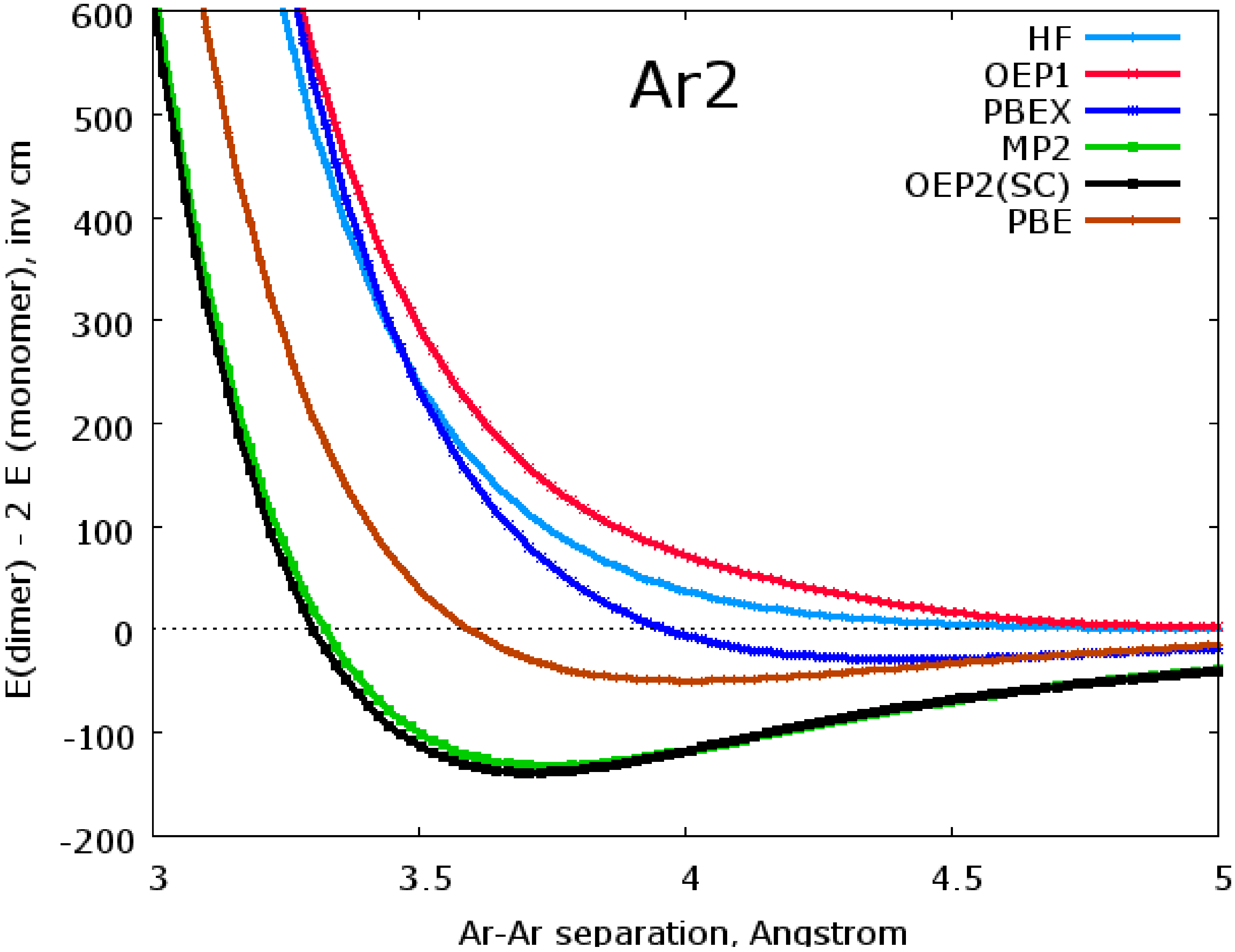
OEPx MAE=0.93 eV

WHAT ABOUT WEAK INTERACTIONS?

The bane of all dft methods...



Ne dimer potential energy
CCSD(T)
MP2
CCSD
OEP−MBPT(2−fsc)
OEP−MBPT(2−ks)
Energy [cm^{-1}]
300
250
200
200
160
100
0
50
−100
−50
−200
−100
−360
5
5.5
6
6.5
7
7.5
8
r [a.u]

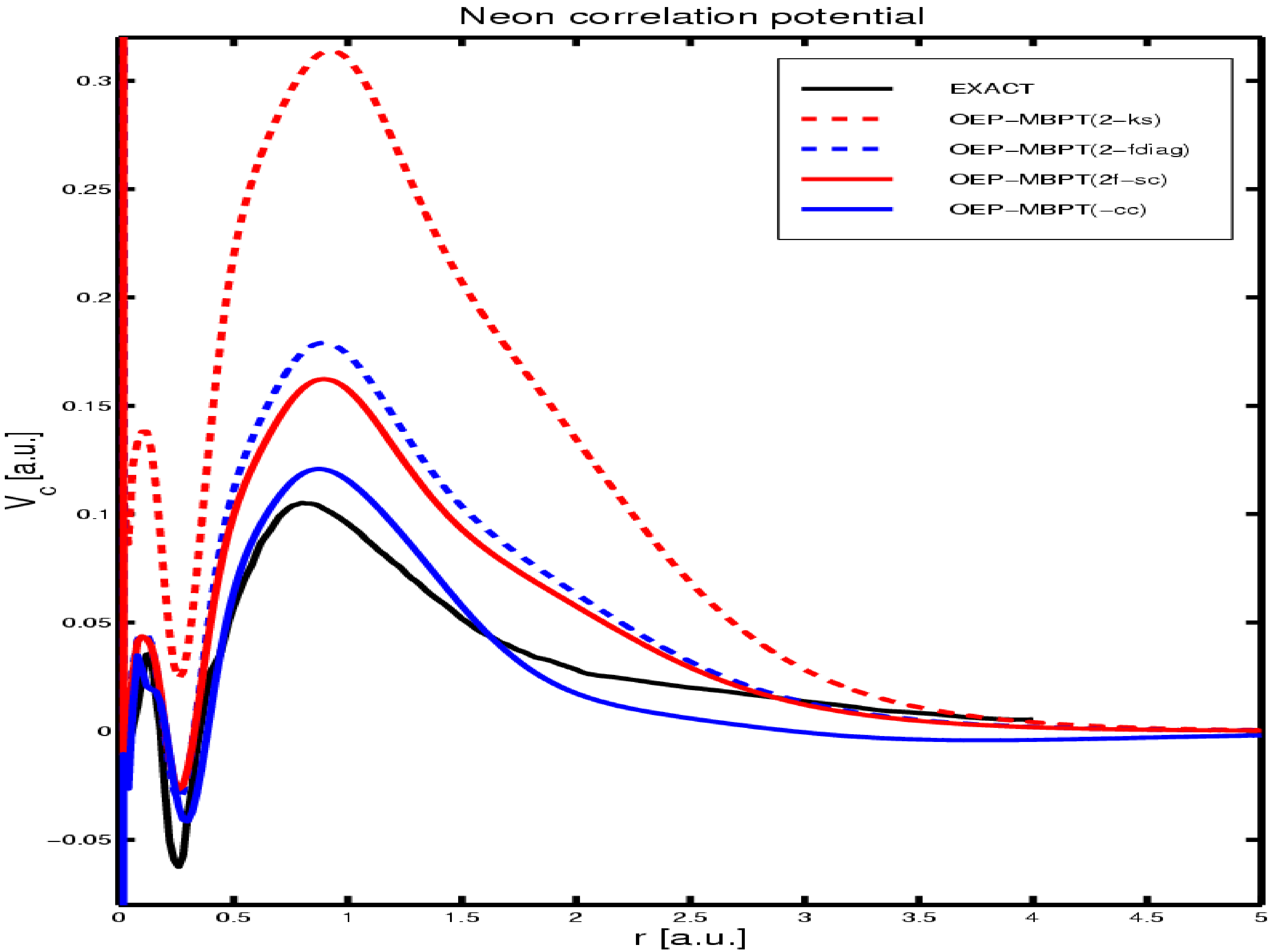

Ar2
HF
OEP1
PBEX
MP2
OEP2(SC)
PBE
E(dimer) - 2 E (monomer), inv cm
600
500
400
300
200
100
0
-100
-200
3
3.5
4
4.5
5
Ar-Ar separation, Angstrom

INFINITE ORDER EFFECTS…

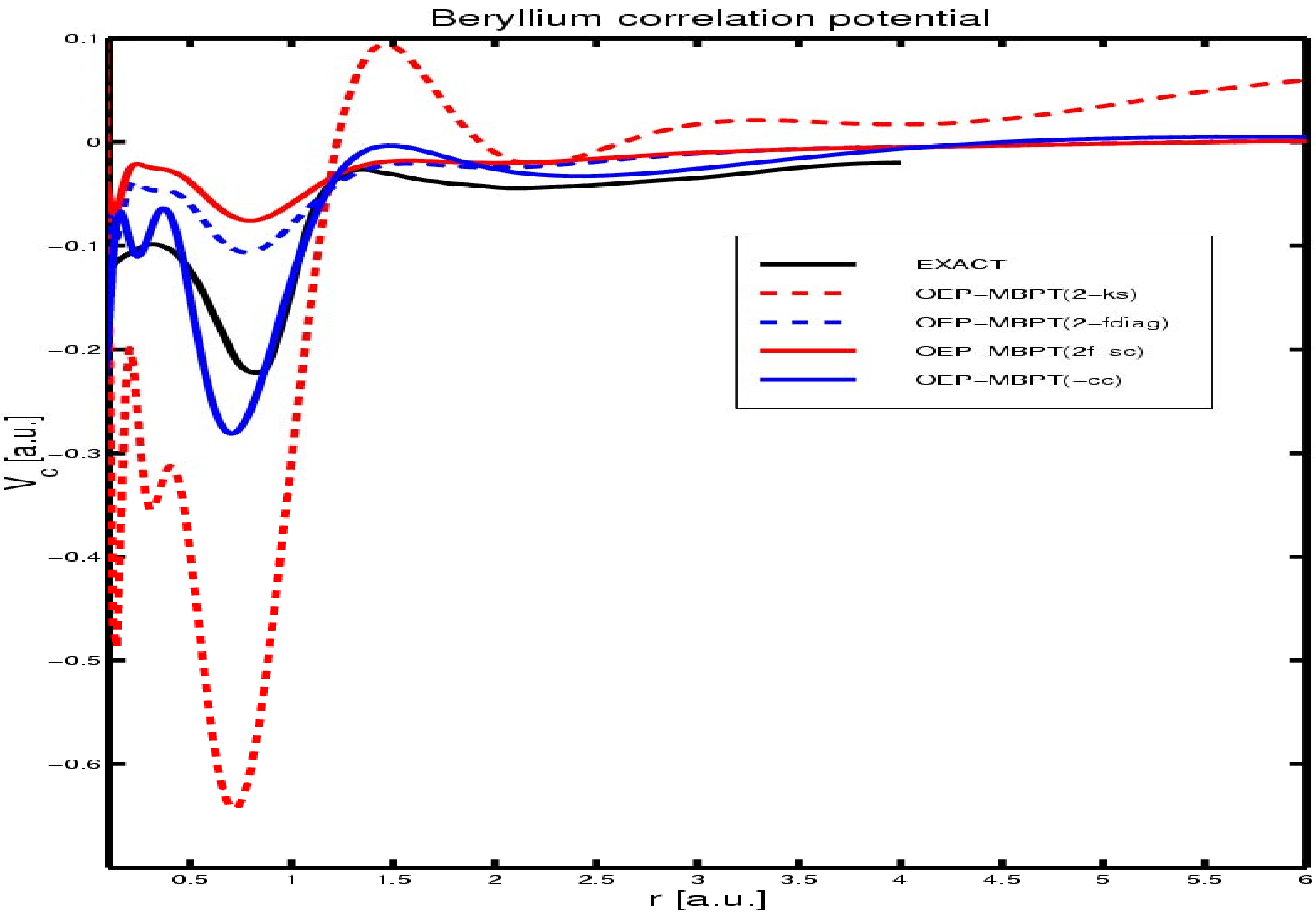
All of our expressions for the density and energies are written in terms of CC amplitudes.

When we do OEP2sc, we limit ourselves to a modifed, but second-order approximation.

If we simply replace second-order t by $t^{(\infty)}$ in this case, taken from LCCSD, we're in a position to explore what happens as we move to the exact OEP result.



Exact QMC result from Umrigar, Gonze.


Beryllium correlation potential
V_c [a.u.]
r [a.u.]
0.1
0
−0.1
−0.2
−0.3
−0.4
−0.5
−0.6
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
5.5
6
EXACT
OEP−MBPT(2−ks)
OEP−MBPT(2−fdiag)
OEP−MBPT(2f−sc)
OEP−MBPT(−cc)

CONCLUSIONS

- The OEP, *ab initio dft,* procedure provides a seamless connection between *ab initio correlated WFT* and DFT*.*
- It solves the self-interaction problem, and gives the correct long-range behavior of $V_{XC.}$
- It provides multiplicative potentials, even though the corresponding orbtial dependent functional is *non-local.* We can plot those potentials to see that they are correct, unlike nearly all other potentials that have been used in standard DFT methods.
- Using the OEP procedure for correlation and for exchange guarantees that the potentials match, so our correlation potential is ideally suited to exact local or non-local exchange. In fact, either (or any combination) is readily accomodated in a fully self-consistent mode.
- Only such an approach introduces dispersion naturally as an inevitable consequence of a proper dft calculation, as opposed to being an add-on to the functional or a post DFT estimate of $C_{6.}$.
- Hence, *ab initio dft* should provide seamless results between weak and strong bonds, ionic and covalent, etc.
- Furthermore, we readily see how to go to any order of PT or to infinite order, ala CC theory to converge to the full CI results. (This, of course, is not recommended!)

CONCLUSIONS (problems?)

- **Energy functional is 2-particle type, so OEP2-sc just rotates orbitals, albiet with the right potential. To get the energy, have to evaluate functional from those OEP2-sc orbitals**
- **1-particle form gives reasonable approximate principal Ip's, and excellent zeroth-order electronic excitation spectra, but *needs an extensive basis that can describe the Rydberg orbitals to achieve the benefits.***
- **The complexity of the OEP2 kernel is excessive, suggesitng that this is NOT the way to do *ab initio dft* excited states, but we have done it, Bokhan, RJB PRA (2006). It is the current benchmark.**
- **TDDFT, and *ab initio dft* , needs to describe charge-transfer states *even with local potentials.***
- **Computation of OEP2 scales ~n^2N^3 compared to density fitted DFT ~$(n+N)^3$, except size of effective basis can be smaller for DFT.**
- **Unlike KS DFT, *ab initio dft* can be extended beyond local potentials, where extra degree of freedom can be used to improve one-particle properties other than density, like Ip's, Ea's, and energy bands.**

Property	GGA/Hybrid Methods	*Ab initio* dft
Convergence to Exact Answer	No	Yes
Correct Self-Interaction	No	Yes
Correct Behavior of Exchange	No	Yes
Correct Behavior of Correlation	No	Yes
Approximation for All Ionization Potentials	No	Yes
Rydberg Excitations	No	Yes
Potential Energy Curves to Dissociation	No	(?)
Weak Interactions	No	Yes

H2O: HOMO and LUMO energies

Method	E(HOMO), eV	E(LUMO), eV	Gap, eV
HF	-13.85	0.81	14.66
HF+OEP2(NLX)	-11.77	0.795	12.56
OEPX(SC)	-14.42	-5.99	8.43
OEPX+OEP2(SC)	-12.52	-5.58	6.94
EOM-CCSD	-12.51(IP)	0.65 (EA)	7.54 (EE)

13.16 (Ip-Ea)