THE RPA IN A DENSITY FUNCTIONAL CONTEXT, AND ITS SEMI-LOCAL CORRECTION

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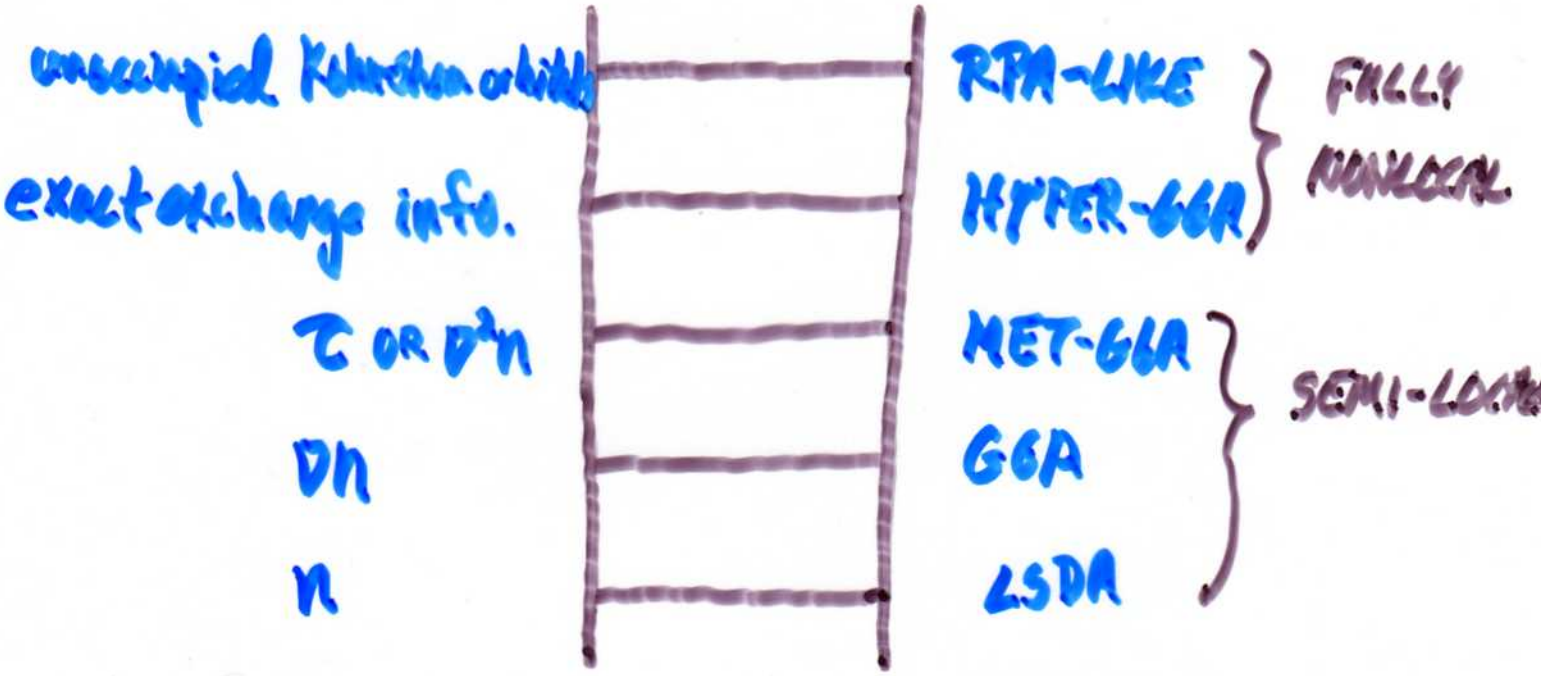
"RPA OLD GUARD"

MORE-INCLUSIVE JACOB'S LADDER OF DENSITY FUNCTIONAL APPROXIMATIONS

$$E_{xc}[n_\uparrow, n_\downarrow] = \int d^3r \, f_{xc}(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow, \tau_\uparrow, \tau_\downarrow, \ldots)$$



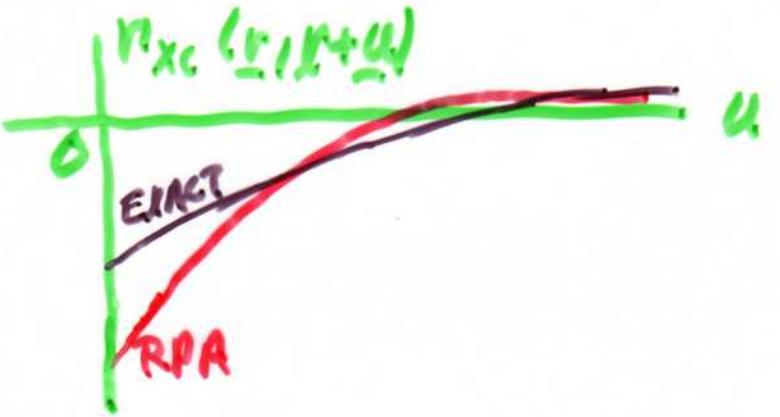
THE SEMI-LOCAL FUNCTIONALS HAVE NON-EMPIRICAL CONSTRUCTIONS, BY CONSTRAINT SATISFACTION.

SO FAR, SUCCESSFUL HYPER-GGA'S HAVE REQUIRED AT LEAST ONE EMPIRICAL PARAMETER.

WHAT DO WE STILL NEED TO UNDERSTAND?

THE RANDOM PHASE APPROXIMATION (RPA) WAS DEVELOPED FOR THE UNIFORM ELECTRON GAS BY BOHM + PINES IN THE 1950's. IT YIELDS A FINITE CORRELATION ENERGY BY SUMMING A SUBSERIES OF DIVERGENT PERTURBATION TERMS TO INFINITE ORDER IN e^2. ITS EXCHANGE ENERGY IS EXACT, BUT ITS CORRELATION ENERGY IS TOO LOW BY ~ 0.02 HARTREE / ELECTRON FOR TYPICAL VALENCE-ELECTRON OR CORE-ELECTRON DENSITIES.

BY NEGLECTING EXCHANGE EFFECTS OF ORDER e^4 AND HIGHER, RPA MAKES THE CORRELATION HOLE DENSITY TOO DEEP NEAR AN ELECTRON.



RPA MAKES A TIME-DEPENDENT HARTREE APPROXIMATION FOR THE DENSITY RESPONSE FUNCTION χ, AND COULD BE BASED ON HARTREE ORBITALS. FOR THE UNIFORM GAS, THE HARTREE AND KOHN-SHAM ORBITALS ARE IDENTICAL.

IN 1975-80, LANGRETH & PERDEW (LP) EXTENDED THESE IDEAS TO NONUNIFORM DENSITIES, PRODUCING EXACT + RPA EXPRESSIONS FOR THE EXCHANGE-CORRELATION ENERGY $E_{xc}[n_+, n_-]$.

COUPLING-CONSTANT INTEGRATION

$$\hat{H}_\lambda \Psi_\lambda = E_\lambda \Psi_\lambda$$

$$E_1 = E_0 + \int_0^1 d\lambda \, \langle \Psi_\lambda | \left(\frac{\partial \hat{H}_\lambda}{\partial \lambda} \right) | \Psi_\lambda \rangle$$

THE DENSITY $n_\lambda(\mathbf{r})$ CAN VARY WITH λ, BUT LP PROPOSED TO MAKE $n_\lambda(\mathbf{r}) = n_1(\mathbf{r}) = n(\mathbf{r})$.

$$\hat{H}_\lambda = \sum_{i=1}^{N} -\tfrac{1}{2}\nabla_i^2 + \sum_{i=1}^{N} v_\lambda(\mathbf{r}_i) + \tfrac{1}{2} \sum_{i \neq j}^{N} \frac{\lambda}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$\lambda = 1$: REAL SYSTEM

$\lambda = 0$: KOHN-SHAM NON-INTERACTING SYSTEM.

$$E_{xc}^{\text{exact}}[n_1,n_\downarrow] = \frac{1}{2}\int d\vec{r}\, n(\vec{r}) \int d\vec{r}\,' \frac{n_{xc}(\vec{r},\vec{r}\,')}{|\vec{r}\,'-\vec{r}|}$$

$$n_{xc}(\vec{r},\vec{r}\,') =$$

$$\int_0^1 d\lambda \langle \Psi_\lambda | [\hat{n}(\vec{r}) - n(\vec{r})][\hat{n}(\vec{r}\,') - n(\vec{r}\,')] - n(\vec{r})\,\delta(\vec{r}\,'-\vec{r}) | \Psi_\lambda \rangle$$

= DENSITY AT $\vec{r}\,'$ OF XC HOLE AROUND AN ELECTRON AT $\vec{r}$.

BY HOLDING $n_\lambda(\vec{r})$ FIXED, WE GET THE SIMPLEST EXPRESSION FOR E_{xc}, WHICH IS MANIFESTLY A FUNCTIONAL OF $n(\vec{r})$.

FLUCTUATION-DISSIPATION THEOREM

$$\langle \Psi_\lambda | [\hat{n}(\vec{r}) - n(\vec{r})][\hat{n}(\vec{r}\,') - n(\vec{r}\,')] | \Psi_\lambda \rangle$$

$$= -\frac{1}{\pi}\int_0^\infty d\omega\, \mathrm{Im}\,\chi_\lambda(\vec{r},\vec{r}\,',\omega)$$

$$\delta n_\lambda(\vec{r},\omega) = \int d\vec{r}\,' \chi_\lambda(\vec{r},\vec{r}\,',\omega)\,\delta v_{ext}(\vec{r}\,',\omega)$$

"RPA IN A DENSITY FUNCTIONAL CONTEXT"

$$\chi_\lambda = \chi_0 + \chi_0 V_\lambda \chi_\lambda$$

= HARTREE APPROX. TO χ_λ.

χ_0 REQUIRES THE OCCUPIED AND UNOCCUPIED KOHN-SHAM ORBITALS. THE χ_c TERM GIVES EXACT EXCHANGE, USING THE EXACT DENSITY INSTEAD OF THE TDU-DIPOLE HARTREE DENSITY PROBABLY IMPROVES χ_λ.

LP ARGUED THAT, AT LEAST FOR THE JELLIUM SURFACE (AS FOR THE UNIFORM GAS), RPA IS CORRECT FOR $n_{xc}(\underline{r}, \underline{r}')$ AT LONG-RANGE ($u = |\underline{r}' - \underline{r}| \to \infty$), WHILE BEYOND-RPA LSDA IS EXACT* AT SHORT-RANGE ($u \to 0$). THIS SUGGESTED THAT THE CORRECTION TO RPA IS A SHORT-RANGE EFFECT WELL-DESCRIBED BY LSDA OR GGA.

* JUST ACCURATE, NOT EXACT:

BURKE, PERDEW & LANGRETH 1994.

PERDEW + WANG 1992 CONSTRUCTED AN ANALYTIC MODEL FOR THE BEYOND-RPA (EXACT) XC HOLE $n_{xc}(\underline{r}, \underline{r}')$ OF A UNIFORM GAS.

THE MODEL INCLUDES:

LONG-RANGE BEHAVIOR FROM RPA

SHORT-RANGE FROM ON-TOP VALUE AND CUSP.

INTEGRAL CONSTRAINTS: PARTICLE AND ENERGY SUM RULES.

PERDEW, BURKE + WANG 1996 CONSTRUCTED A BEYOND-RPA GGA BY ADDING THE SECOND-ORDER GRADIENT TERM IN $n_{xc}(\underline{r}, \underline{r}')$, THEN CUTTING OFF THE SPURIOUS CONTRIBUTIONS TO SATISFY EXACT HOLE CONSTRAINTS

YAN, PERDEW + KURTH 2000 CONSTRUCTED A WITHIN-RPA UNIFORM GAS HOLE AND THEREFROM AN RPA GGA.

THEY PROPOSED THE RPA+ APPROXIMATION

$$E_{xc}^{RPA+} = E_{xc}^{RPA} + \{E_c^{sl} - E_c^{sl,RPA}\},$$

WHERE sl = SEMILOCAL = LSDA OR GGA.

THE CORRECTION WAS FOUND TO BE $\sim +0.02$ HARTREE/ELECTRON, IN BOTH LSDA AND GGA. IT GREATLY IMPROVED (OVER RPA) THE TOTAL ENERGIES OF ATOMS, AND THEIR IONIZATION ENERGIES (JIANG + ENGEL 2007).

THE SEMI-LOCAL CORRECTION TO RPA ATOMIZATION ENERGIES WAS FOUND TO BE ALMOST ZERO, BECAUSE MOLECULES + THEIR CONTITUENT ATOMS HAVE THE SAME NUMBER OF ELECTRONS (AT NORMAL DENSITIES).

YPK 2009 THEREFORE EXPECTED THAT RPA AND RPA+ ATOMIZATION ENERGIES WOULD BE ACCURATE. IT WAS PUZZLING WHEN FURCHE 2001 FOUND THAT RPA AND RPA+ ATOMIZATION ENERGIES ARE TOO LOW, TYPICALLY BY 10 kcal/mol.

"RPA ATOMIZATION ENERGY PUZZLE"

RPA ATOMIZATION ENERGIES CAN BE IMPROVED VIA EMPIRICAL RANGE SEPARATION:

SHORT-RANGE: LSDA OR GGA

LONG-RANGE: RPA

(ÁNGYÁN, TOULOUSE, SCUSERIA)

RUZSINSZKY, PERDEW, & CSONKA 2010 CONCLUDED THAT THE CORRECTION TO RPA IN A MOLECULE HAS INTERMEDIATE RANGE AND THUS IS FULLY NONLOCAL. THEIR EMPIRICAL HYBRID $(0.5\,\mathrm{RPA}+)+(0.5\,\mathrm{GGA\ PBE})$ WORKED RATHER WELL FOR ATOMIZATION ENERGIES.

THIS SUGGESTS THAT THE RPA OR RPA+ CORRELATION HOLE DOES NOT CANCEL ENOUGH OF THE PART OF THE EXACT EXCHANGE HOLE THAT EXTENDS FROM ONE ATOM TO THE NEXT.

OPEN QUESTIONS:

CAN WE MAKE A NONEMPIRICAL HYPER-GGA, EITHER AS A STAND-ALONE FUNCTIONAL FOR E_{xc} OR AS A CORRECTION TO RPA?

DO WE KNOW ENOUGH TO DO THIS?

WHAT IS THE CORRECT UNIVERSAL LONG-RANGE ($|\underline{r}-\underline{r}'| \to \infty$) BEHAVIOR OF $v_{xc}^{exact}(\underline{r},\underline{r}')$?

EXACT EXCHANGE : NOT FOR THE JELLIUM SURFACE

RPA : NOT FOR STRETCHED H_2^+

CANCELLATION OF X & C : NOT FOR STRETCHED H_2^+

MINIMALLY-CORRELATED WAVEFUNCTION (SAVIN, GORI-GIORGI, STOLL)

HOW GOOD ARE MORE-ADVANCED RPA-LIKE FUNCTIONALS ?

RPA + SOSEX (SCUSERIA, KRESSE)

RPAE (VON BARTH)

ISTLS (DOBSON) HFB (SCUSERIA)

NONLOCALITY IS HARD.
STRETCHED BONDS ARE HARD.

APPENDIX : COMMENT ON RANGE-SEPARATED HYBRIDS WITH FULL EXACT EXCHANGE AT LONG-RANGE (E.G., LCωPBE)

MODEL $n_{x_c}(\underline{r}_1,\underline{r}_1') = [1-\mathrm{erf}(\omega|\underline{r}_1-\underline{r}_1'|)]\, n_x^{GGA}(\underline{r}_1,\underline{r}_1')$

$+\,\mathrm{erf}(\omega|\underline{r}_1-\underline{r}_1'|)\, n_x^{exact}(\underline{r}_1,\underline{r}_1') + n_c^{GGA}(\underline{r}_1,\underline{r}_1')$

NEARLY MANY-ELECTRON SELF-INTERACTION FREE

IF ω IS FITTED SEMIEMPIRICALLY TO BEYOND- AND WITHIN-RPA ATOMIZATION ENERGIES, THIS MIGHT GIVE A GOOD CORRECTION TO RPA.

BUT, IF $\omega(\underline{r}_1)$ IS CHOSEN NONEMPIRICALLY TO SATISFY $\int d^3r_1'\, n_{x_c}(\underline{r}_1,\underline{r}_1') = -1$, THEN THIS GIVES THE RPA+ CORRECTION TO RPA ATOMIZATION ENERGIES.