Hierarchies of Pertubation Theories as Post-Hartree-Fock and Post-Kohn-Sham shemes and a Jacob's Ladder for Pauli kinetic energy density functional approximations

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22.1.2024

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ABSTRACT A hierarchy and comparison of pertubation theories (PT) as Møller-Plesset (MP) pertubation theory, pertubation theory along the adiabatic-connection (AC) such as Görling-Levy pertubation theory (GLPT) and the Pertubation theory along the Pauli contribution by Redeker is presented with a classification as post-Hartree-Fock (HF) and post-Kohn-Sham (KS) method relative to their fundamental framework. Lastly a Jacob's Ladder is given for approximating the Pauli kinetic energy density functional (KEDF).

I. MØLLER-PLESSET (MP) PERTUBATION THEORY AS A POST-HARTREE-FOCK (HF) APPROACH

Møller-Plesset (MP) pertubation theory [2] is a post-Hartree-Fock (HF) method. It improves the HF method [9], [10] by the means of Rayleigh-Schrödinger pertubation theory (RSPT). We consider the unpertubated Hamiltonian as the Fock operator $\hat{H}(\lambda = 0) = \hat{F}$ and the pertubation as the so called shifted Fock operator with the parameter $0 \leq \lambda \leq 1$

$$\hat{H}(\lambda) = \hat{F} + \lambda\left[\hat{H} - \hat{F}\right] \tag{1}$$

We consider the many-body Fock operator $\hat{F} = \sum_{k=1}^{N} \hat{f}(k)$ as the sum over the one-electron Fock operators with the Hartree-Fock (HF) equation [9], [10]

$$\hat{f}(k)\phi_i(k) = \left(-\frac{1}{2}\Delta_k + v(k) + v_H(k)\right)\phi_i(k) + v_X^{NL}(k,k')\phi_i(k') = \varepsilon_i(k)\phi_i(k) \tag{2}$$

Where $v_H(k) = \sum_j^{occ} \int dk'\, \phi_j(k')\phi_j(k') f_H(k,k')$ is the Hartree potential, which can be rewritten in terms of the density in Density functional theory (DFT) [3], [4], and $v_X^{NL}(k,k')\phi_i(k') = \int dk'\, \gamma(k,k') f_H(k,k')\phi_i(k')$ is the nonlocal exchange potential acting on the i-th HF orbital depending on the density matrix $\gamma(k,k') = \sum_j^{occ} \phi_j(k)\phi_j(k')$, which is an Integraloperator, thus transforming the HF equations into a set of Integro-Differential equations. We see that for $\lambda = 1$ the Hamiltonian $\hat{H}(\lambda = 1) = \hat{H} = \hat{T} + \hat{v} + \hat{V}_{ee}$ turns into the electronic Hamiltonian with full electron-electron interaction. We can also see that the shifted Fock operator becomes

$$\left[\hat{H} - \hat{F}\right] = \hat{V}_{ee} - \sum_k [v_H(k) + v_X^{NL}(k)] \tag{3}$$

With $\hat{V}_{ee} = \sum_{k<j} r_{kl}^{-1}$. We get in 1st order pertubation theory

$$E_1 = \left\langle \Phi^{HF} \middle| \hat{H} - \hat{F} \middle| \Phi^{HF} \right\rangle = -\frac{1}{2}\sum_{i,j} [(ii|jj) - (ij|ji)] \tag{4}$$

Thus

$$E_0 + E_1 = \left\langle \Phi^{HF} \middle| \hat{F} \middle| \Phi^{HF} \right\rangle + \left\langle \Phi^{HF} \middle| \hat{H} - \hat{F} \middle| \Phi^{HF} \right\rangle = \left\langle \Phi^{HF} \middle| \hat{H} \middle| \Phi^{HF} \right\rangle = E_0^{HF} \tag{5}$$

The Hartree-Fock (HF) energy back. This phenomenon is typical for post-HF methods. The Configuration Interaction (CI) method with singly (S) excited Slater determinants $\Psi^{CIS} = \sum_{i=0}^{1} c_I \Phi_i = c_o \Phi^{HF} + c_1 \Phi_i^a = \Phi^{HF}$ due to Brillouin's theorem $\langle \Phi^{HF} | \hat{H} | \Phi_i^a \rangle = 0$. The first meaningful correction to the Hartree-Fock (HF) energy is obtained in Møller-Plesset pertubation theory 2nd order (MP2) as

$$E^{MP2} = E_0 + E_1 + E_2 = E_0^{HF} + \frac{1}{2} \sum_{i,j}^{occ} \sum_{a,b}^{unocc} \frac{(ia|jb)(ai|bj) - (ia|jb)(aj|bi)}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \tag{6}$$

In principle also higher methods such as MP3 and MP4 could be calculated, but note, that there is no guarantee, that MP pertubation theory with higher orders converges.

II. PERTUBATION THEORY ALONG THE ADIABATIC CONNECTION (AC) AND PERTUBATION THEORY ALONG THE PAULI CONTRIBUTION AS POST-KOHN-SHAM (KS) METHODS

If we interchange in Møller-Plesset (MP) pertubation theory [2] the Fock operator $\hat{F}$ with the many-body KS Hamiltonian $\hat{H}(\alpha = 0) = \hat{H}_S = \sum_{i=1}^{N} \hat{h}_S(i) = \hat{T} + \hat{v}_S$ and the shifted Fock operator with the electron-electron interaction as the pertubation $\hat{V}_{ee} = \sum_{k<j} r_{kl}^{-1}$ we arrive at pertubation theory along the adiabatic connection (AC) [5],[6], which can therefore be regarded as a post Kohn-Sham (KS) method with the coupling strength $0 \leq \alpha \leq 1$

$$\hat{H}(\alpha) = \hat{T} + \hat{v}(\alpha) + \alpha \hat{V}_{ee} \tag{7}$$

Notice that for $\hat{H}(\alpha = 1) = \hat{T} + \hat{v} + \hat{V}_{ee} = \hat{H}$ the electronic Hamiltonian arises as in MP pertubation theory. If set again the unpertubated Hamiltonian as the KS Hamiltonian

$$\hat{H}(\beta = 0) = -\frac{1}{2}\Delta + v(r) + v_{HXC}(r) = \hat{h}_S \tag{8}$$

But this time choose as the pertubation the Pauli potential $v_P(r)$ instead of the electron-electron interaction $\hat{V}_{ee}$ we arrive at the post-KS pertubation theory Ansatz by Redeker [1] with $0 \leq \beta \leq 1$

$$\hat{H}(\beta) = \frac{1}{2}\Delta + v(r) + v_{HXC}(r) + \beta v_P(r) \tag{9}$$

Hierarchies of PT	**Post Hartree-Fock (HF) method**	**Post Kohn-Sham (KS) methods**	
	Møller-Plesset (MP) pertubation theory [2]	**Pertubation theory along the Adiabatic-Connection (AC)/Görling-Levy(GLPT) [11],[12],[5],[6]**	**Pertubation theory along the Pauli contribution by Redeker [1]**
	$0 \leq \lambda, \alpha, \beta \leq 1$		
$\hat{H}(0)$	**Fock** operator $\hat{F}$	Many-body **KS** Hamiltonian $\hat{H}_S$	One-electron **KS** Hamiltonian $\hat{h}_S$
$\hat{H}(1)$	$\hat{H}$	$\hat{H}$	$\frac{1}{2}\Delta + v(r) + v_{HXC}(r) + v_P(r)$
$\Psi(0)$	**HF** determinant Φ^{HF}	**KS** determinant Φ^{KS}	**KS** orbital $\phi_i(r)$
$\Psi(1)$	Electronic GS wavefunction Ψ_0		Root of density $\sqrt{\varrho(r)} \overset{HK}{\Leftrightarrow} \Psi_0$
E_1	**HF** energy and orb. energy $E_0^{HF} - \langle \Phi^{HF} \vert \hat{F} \vert \Phi^{HF} \rangle$	$\langle \Phi^{KS} \vert \hat{V}_{ee} \vert \Phi^{KS} \rangle = V(\alpha)\vert_{\alpha=0} = E_{\boldsymbol{HX}}[\varrho]$	$\varepsilon_1 = \langle \phi_i \vert v_{\boldsymbol{P}}(r) \vert \phi_i \rangle = \frac{d\varepsilon_i(\beta)}{d\beta}\Big\vert_{\beta=0}$
E_j mit $j > 2$	MPj with correlation $E_C = E^{MPj}$	$E_C[\varrho] = \sum_{j=2}^{\infty} E_j = \int_0^1 d\alpha\, V(\alpha) = E_C(\alpha = 1) - E_C(\alpha = 0) = E_C^{AC}[\varrho]$ mit $V(\alpha) = \langle \Psi(\alpha) \vert \hat{V}_{ee} \vert \Psi(\alpha) \rangle = \frac{dE(\alpha)}{d\alpha}$	GAC theorem for the Pauli KEDF (PT contains intrinsic correlation through KS formalism) by Redeker [1] $T_P^{GAC}[\varrho] = -\int_0^1 d\beta\, \frac{dT(\beta)}{d\beta} = T(\beta = 0) - T(\beta = 1) = = T_S[\varrho] - T_W[\varrho]$

Table 1: Hierarchies of Pertubation Theories (PT) as Post-Hartree-Fock (HF) & Kohn-Sham (KS) shemes

We get in 1st order pertubation theory along the adiabatic connection (AC) the Hartree-exchange energy back

$$E_1 = \left\langle \Phi^{KS} \middle| \hat{V}_{ee} \middle| \Phi^{KS} \right\rangle = E_{HX} \tag{10}$$

III. JACOB'S LADDER FOR PAULI KINETIC ENERGY DENSITY FUNCTIONAL APPROXIMATIONS

In Orbital-free density functional theory (OFDFT) the focus lies on approximating the Pauli (P) Kinetic energy density functional (KEDF) $T_P[\varrho]$ instead of approximating the Exchange-correlation DF $E_{XC}[\varrho]$.We therefore propose a new Jacob's Ladder in the spirit of Perdew and Schmidt [14]. The first three rungs would be identical as for the first rung the Local Density Aprroximation (LDA) in form of the Thomas-Fermi (TF) functional will be employed for approximating the Pauli KEDF. As a second and third rung as Generalized Gradient Approximation (GGA) or meta-GGA the von Weizsäcker (W) functional holds as an Pauli Kinetic Energy Density functional approximation (PKEDFA) [13]. The fourth rung would be several nonlocal KEDF such e.g. the Huang-Carter (HC) functional [15],[16], or the Mi-Genova-Pavanello (MGP) functional [17] or the Wang-Teter (WT) functional [18],[19]. The general form of a Nonlocal KEDF with the arbitrary fractional exponents ζ and η and the nonlocal KEDF kernel f_{NL}^{KEDF} is

$$T_{NL}[\varrho](r,r') = \iint dr\, dr' \varrho^{\zeta}(r) f_{NL}^{KEDF}[\varrho](r,r') \varrho^{\eta}(r') \tag{11}$$

This corresponds to Hybrid functionals in the regular Jacob's Ladder [14] since the HF exchange is also nonlocal. The fifth rung of the ladder of PKEDFA would be those explicitly orbital-dependent such as the KS Kinetic energy $T_S[\varrho] = \sum_{i=1}^{N} \left\langle \phi_i \middle| -\frac{1}{2}\Delta \middle| \phi_i \right\rangle = \frac{1}{2}\sum_{i=1}^{N} \int dr\, |\nabla \phi_i(r)|^2$ and the GAC theorem by Redeker [1] $T_P^{GAC}[\varrho] = -2\int_0^1 d\beta \sum_{i=1}^{N} \left\langle \frac{d\phi_i}{d\beta} \middle| -\frac{1}{2}\Delta \middle| \phi_i \right\rangle$

Rung	**Jacob's Ladder for $E_{XC}[\varrho]$ DFA**	**Jacob's Ladder for $T_P[\varrho]$ PKEDFA**
5th	RPA, ACFD and beyond with PT $E_C^{ACFD/RPA}[\phi_i^{occ}, \phi_a^{unocc}]$	KS KEDF $T_S[\varrho] = \frac{1}{2}\sum_{i=1}^{N} \int dr\, \|\nabla \phi_i(r)\|^2$ GAC theorem $T_P^{GAC}[\varrho]$
4th	Hybrid functionals (with NL HFX) $E_C^{GGA} + (1-\lambda)E_X^{GGA} + \lambda E_X^{HF}[\phi_i^{occ}]$	Nonlocal (NL) KEDF $T_{NL}[\varrho](r,r')$
3rd	Meta GGA $E_{XC}^{meta\ GGA}[\varrho] = \int \varepsilon_{meta-GGA}(\varrho, \nabla\varrho, \Delta\varrho)\varrho(r)dr$; von Weizsäcker $T_W[\varrho]$	
2nd	Gradient Gradient Approximation (GGA) $E_{XC}^{GGA}[\varrho] = \int \varepsilon_{GGA}(\varrho, \nabla\varrho)\varrho(r)dr$	
1st	Local Density Approximation (LDA) $E_X^{LDA}[\varrho] = -C_X \int dr\, \varrho^{4/3}$; $T_{TF}[\varrho] = C_{TF} \int dr\, \varrho^{5/3}$	

Table 2: Jacob's Ladder for Pauli kientic energy density functional approximations (PKEDFA)

IV. CONCLUSION AND OUTLOOK

A hierarchy of MP pertubation theory, PT along the AC, PT along the Pauli contribution and a classification as post-HF or post-KS method is given. A Jacob's Ladder sheme [14] instead of approximating the exchange-correlation (XC) energy for approximating the Pauli (P) Kinetic energy density functional (KEDF) is sketched.

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