Second order Kohn-Sham perturbation theory:  
Asymptotic properties of correlation potential for finite systems

Eberhard Engel, J.W.Goethe-Universität Frankfurt

Many thanks to collaborators:  
Hong Jiang
Andreas Facco Bonetti

and to DFG for financial support
Introduction

Framework for derivation of orbital-dependent $E_C$: Kohn-Sham-based many-body theory leads to MP2-type correlation functional $E_C^{MP2}$ within lowest order perturbation theory.
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Framework for derivation of orbital-dependent $E_c$: Kohn-Sham-based many-body theory → leads to MP2-type correlation functional $E_c^{MP2}$ within lowest order perturbation theory

Attempt to apply $E_c^{MP2}$ to atoms failed: Divergence in asymptotic regime

Facco Bonetti et al., PRL 86, 2241 (2001)
Introduction

Framework for derivation of orbital-dependent $E_c$: Kohn-Sham-based many-body theory
\[ \longrightarrow \text{leads to MP2-type correlation functional } E_{c}^{\text{MP2}} \text{ within lowest order perturbation theory} \]

Attempt to apply $E_{c}^{\text{MP2}}$ to atoms failed: Divergence in asymptotic regime
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On the other hand: $v_{c}^{\text{MP2}}(r \to \infty) \sim \alpha/r^4$

Niquet et al., JCP 118, 9504 (2003)
OPM equation for spherical, spin-saturated, closed-subshell systems

\[
\int_0^\infty dr' K(r, r') v(r') = Q^a(r) + Q^b(r)
\]

\[
K(r, r') = -2 \sum_{nl} \Theta_{nl} P_{nl}(r) G_{nl}(r, r') P_{nl}(r') \quad \text{occupied } nl \text{ only!}
\]

\[
Q^a(r) = -\sum_{nl} \int_0^\infty dr' P_{nl}(r) G_{nl}(r, r') \frac{\delta E}{\delta P_{nl}(r')}
\]

\[
Q^b(r) = \sum_{nl} P_{nl}(r)^2 \frac{\partial E}{\partial \epsilon_{nl}}
\]

\[
G_{nl}(r, r') = \sum_{n' \neq n} \frac{P_{n'l}(r) P_{n'l}(r')}{\epsilon_{n'l} - \epsilon_{nl}}
\]

\[
\Theta_{nl} = \begin{cases} 
2(2l + 1) & \text{for } \epsilon_{nl} \leq \epsilon_F \\
0 & \text{otherwise}
\end{cases}
\]

\[\rightarrow\]\ clear for systems with only discrete spectrum, but what about continuum states?
Continuum states: Basics

Standard positive energy solutions for \( v_s(r \to \infty) = 0 \) (atomic units)

\[
\left\{ \frac{\partial^2}{\partial r^2} - \frac{l(l + 1)}{r^2} + k^2 - 2v_s(r) \right\} P_{kl}(r) = 0
\]

with \( k = (2\epsilon)^{1/2} \)

\[
P_{kl}(r \to \infty) \sim \sqrt{\frac{2}{\pi}} \sin \left[ kr + \frac{Z}{k} \ln(2kr) - \frac{\pi}{2} l - \eta_{kl} \right]
\]

\( (v_s(r \to \infty) \sim -\frac{Z}{r}) \)
Continuum states: Basics

Standard positive energy solutions for \( v_s(r \to \infty) = 0 \) (atomic units)

\[
\left\{ \frac{\partial^2}{\partial r^2} - \frac{l(l + 1)}{r^2} + k^2 - 2v_s(r) \right\} \mathcal{P}_{kl}(r) = 0 \\
\mathcal{P}_{kl}(r \to \infty) \sim \sqrt{\frac{2}{\pi}} \sin \left[ kr + \frac{Z}{k} \ln(2kr) - \frac{\pi}{2}l - \eta_{kl} \right] \quad (v_s(r \to \infty) \sim -\frac{Z}{r})
\]

Completeness and orthonormality

\[
\sum_n P_{nl}(r) P_{nl}(r') + \int_0^\infty dk \mathcal{P}_{kl}(r) \mathcal{P}_{kl}(r') = \delta(r - r')
\]

\[
\int_0^\infty dr P_{nl}(r) \mathcal{P}_{kl}(r) = 0 \quad \int_0^\infty dr \mathcal{P}_{kl}(r) \mathcal{P}_{k'l}(r) = \delta(k - k')
\]

Functional derivative

\[
\frac{\delta \mathcal{P}_{kl}(r)}{\delta \mathcal{P}_{k'l}(r')} = \delta(k - k') \delta(r - r')
\]
MP2 energy including continuum states (Kelly, 1963)

\[ E_{\text{MP2}} = \sum_{n_1n_2n_3n_4}^{l_1l_2l_3l_4} \frac{N(n_1l_1, n_2l_2|n_3l_3, n_4l_4)}{\epsilon_{n_1l_1} + \epsilon_{n_2l_2} - \epsilon_{n_3l_3} - \epsilon_{n_4l_4}} + 2E_{\text{DC}} + E_{\text{CC}} \]

\[ E_{\text{DC}} = \sum_{n_1n_2n_3}^{l_1l_2l_3} \int_0^\infty dk \sum_l \frac{N(n_1l_1, n_2l_2|n_3l_3, kl)}{\epsilon_{n_1l_1} + \epsilon_{n_2l_2} - \epsilon_{n_3l_3} - \epsilon} \]

\[ E_{\text{CC}} = \sum_{n_1n_2}^{l_1l_2} \int_0^\infty dk \int_0^\infty dk' \sum_{ll'} \frac{N(n_1l_1, n_2l_2|kl, k'l')}{\epsilon_{n_1l_1} + \epsilon_{n_2l_2} - \epsilon - \epsilon'} \]

\[ N(12|34) = \Theta_1\Theta_2(1 - \Theta_3)(1 - \Theta_4) \sum_L (12|34)_L \]

\[ \times \left[ V_{l_1l_2,L}^{l_3l_4} (34|12)_L - W_{l_1l_2,L}^{l_3l_4} (34|21)_L \right] \quad (i \equiv n_i l_i) \]

\[ (12|34)_L = \int_0^\infty dr' \int_0^\infty dr'' \frac{r_L^L}{r_{L+1}^L} P_{n_1l_1}(r')P_{n_3l_3}(r')P_{n_2l_2}(r'')P_{n_4l_4}(r'') \]
Handling of continuum states in OPM procedure: I

Complete $G_{nl}$ consists of discrete and continuum states

\[
G_{nl}(r, r') = \sum_{n' \neq n} \frac{P_{n'l}(r) P_{n'l}(r')}{\epsilon_{n'l} - \epsilon_{nl}} + \int_0^\infty dk' \frac{P_{k'l}(r) P_{k'l}(r')}{e' - \epsilon_{nl}}
\]

\[
G_{kl}(r, r') = \sum_{n'} \frac{P_{n'l}(r) P_{n'l}(r')}{\epsilon_{n'l} - \epsilon} + \mathcal{P} \int_0^\infty dk' \frac{P_{k'l}(r) P_{k'l}(r')}{e' - \epsilon}
\]
Handling of continuum states in OPM procedure: I

Complete $G_{nl}$ consists of discrete and continuum states

\[
G_{nl}(r, r') = \sum_{n' \neq n} \frac{P_{n'l}(r) P_{n'l}(r')}{\epsilon_{n'l} - \epsilon_{nl}} + \int_0^\infty dk' \frac{\overline{P}_{k'l}(r) \overline{P}_{k'l}(r')}{\epsilon' - \epsilon_{nl}}
\]

\[
G_{kl}(r, r') = \sum_{n'} \frac{P_{n'l}(r) P_{n'l}(r')}{\epsilon_{n'l} - \epsilon} + \mathcal{P} \int_0^\infty dk' \frac{\overline{P}_{k'l}(r) \overline{P}_{k'l}(r')}{\epsilon' - \epsilon}
\]

Green's functions satisfy differential equations

\[
\begin{cases}
- \frac{1}{2} \left( \frac{\partial^2}{\partial r^2} - \frac{l(l + 1)}{r^2} \right) + v_s(r) - \epsilon_{nl} \bigg) G_{nl}(r, r') = \delta(r - r') - P_{nl}(r)P_{nl}(r') \\
- \frac{1}{2} \left( \frac{\partial^2}{\partial r^2} - \frac{l(l + 1)}{r^2} \right) + v_s(r) - \epsilon \bigg) G_{kl}(r, r') = \delta(r - r')
\end{cases}
\]

Boundary conditions

\[
\int_0^\infty dr' G_{nl}(r, r') P_{nl}(r') = \int_0^\infty dr' G_{kl}(r, r') \overline{P}_{kl}(r') = 0
\]
Handling of continuum states in OPM procedure: II

Green’s function can be expressed in terms of non-normalizable solutions of KS equation

\[
G_{nl}(r, r') = 2 \left\{ \Theta(r - r') P_{nl}(r) S_{nl}(r') + \Theta(r' - r) S_{nl}(r) P_{nl}(r') \right. \\
- P_{nl}(r) \left[ P_{nl}(r') \int_0^{r'} dx P_{nl}(x) S_{nl}(x) + S_{nl}(r') \int_{r'}^\infty dx P_{nl}(x)^2 \right] \\
- P_{nl}(r') \left[ P_{nl}(r) \int_0^r dx P_{nl}(x) S_{nl}(x) + S_{nl}(r) \int_{r}^\infty dx P_{nl}(x)^2 \right] \\
+ 2 P_{nl}(r) P_{nl}(r') \int_0^\infty dx \int_0^x dy P_{nl}(x)^2 P_{nl}(y) S_{nl}(y) \right\}
\]

with

\[
\left\{ \frac{\partial^2}{\partial r^2} - \frac{l(l + 1)}{r^2} + 2[\epsilon_{nl} - v_s(r)] \right\} S_{nl}(r) = 0
\]

\[
P_{nl}(r) S_{nl}'(r) - P_{nl}'(r) S_{nl}(r) = 1
\]
Handling of continuum states in OPM procedure: III

How “complete” is the set of Rydberg states?

![Graph showing the comparison of G_{1S}(r,r) with different n values against r in Bohr units.](image)
Handling of continuum states in OPM procedure: IV

\[
Q^a(r) = Q_-(r) + Q_+(r)
\]

\[
Q_-(r) = -\sum_{nl} \int_0^\infty \int_0^\infty dr' P_{nl}(r) G_{nl}(r, r') \frac{\delta E_{c}^{\text{MP2}}}{\delta P_{nl}(r')} \frac{1}{\Omega}
\]

\[
Q_+(r) = -\sum_{l} \int_0^\infty d\kappa \int_0^\infty dr' \overline{P}_{kl}(r) G_{kl}(r, r') \frac{\delta E_{c}^{\text{MP2}}}{\delta \overline{P}_{kl}(r')} \frac{1}{\Omega}
\]

\[
Q^b(r) = \sum_{nl} P_{nl}(r) \frac{\partial E_{c}^{\text{MP2}}}{\partial \epsilon_{nl}} \quad \text{discrete states only}
\]
Handling of continuum states in OPM procedure: IV

\begin{align*}
Q^a(r) &= Q^a_-(r) + Q^a_+(r) \\
Q^a_-(r) &= - \sum_{nl} \int_0^\infty dr' P_{nl}(r) G_{nl}(r, r') \frac{\delta E_{c}^{\text{MP2}}}{\delta P_{nl}(r')} \\
Q^a_+(r) &= - \sum_{l} \int_0^\infty dk \int_0^\infty dr' \overline{P}_{kl}(r) G_{kl}(r, r') \frac{\delta E_{c}^{\text{MP2}}}{\delta \overline{P}_{kl}(r')} \\
Q^b(r) &= \sum_{nl} P_{nl}(r)^2 \frac{\partial E_{c}^{\text{MP2}}}{\partial \epsilon_{nl}} \quad \text{discrete states only}
\end{align*}

Sum rule?

\begin{align*}
\int_0^\infty dr \int_0^\infty dr' K(r, r') v(r') &= 0 \\
\int_0^\infty dr Q^a(r) &= 0 \\
\int_0^\infty dr Q^b(r) &= 2 \sum_{nl} \frac{\partial E_{c}^{\text{DC}}}{\partial \epsilon_{nl}} \bigg|_{\epsilon_{nl} \neq 0} + \sum_{nl} \frac{\partial E_{c}^{\text{CC}}}{\partial \epsilon_{nl}} \bigg|_{\epsilon_{nl} \neq 0}
\end{align*}
Analysis of OPM equation for \( r \to \infty \): Complete space

Basic assumption: \( v(r \to \infty) = 0 \)

\[ P_{nl}(r) \to A_{nl} r^{\beta_{nl}} e^{-\alpha_{nl}r} \]

\[ S_{nl}(r) \to \frac{1}{2\alpha_{nl}A_{nl}} r^{-\beta_{nl}} e^{\alpha_{nl}r} \]
Analysis of OPM equation for $r \to \infty$: Complete space

Basic assumption: $v(r \to \infty) = 0$

$\rightarrow$ asymptotic behavior of discrete states

$$P_{nl}(r) \rightarrow A_{nl} r^{\beta_{nl}} e^{-\alpha_{nl} r}$$

$$S_{nl}(r) \rightarrow \frac{1}{2\alpha_{nl} A_{nl}} r^{-\beta_{nl}} e^{\alpha_{nl} r}$$

$\rightarrow$ asymptotic behavior of OPM equation: $P_F =$ highest occupied state

$$\int_0^\infty dr' \ K(r, r') \ v(r') \rightarrow \ C \ P_F(r)^2 \ \int_0^r dx \ P_F(x) S_F(x) \ \int_0^\infty dr' \ P_F(r')^2 \ v(r')$$
Analysis of OPM equation for $r \to \infty$: Complete space

Basic assumption: $v(r \to \infty) = 0$

$\longrightarrow$ asymptotic behavior of discrete states

$$
P_{nl}(r) \longrightarrow A_{nl} r^{\beta_{nl}} e^{-\alpha_{nl} r}
$$

$$
S_{nl}(r) \longrightarrow \frac{1}{2\alpha_{nl} A_{nl}} r^{-\beta_{nl}} e^{\alpha_{nl} r}
$$

$\longrightarrow$ asymptotic behavior of OPM equation: $P_F = \text{highest occupied state}$

$$
\int_0^\infty dr' K(r, r') v(r') \longrightarrow C P_F(r)^2 \int_0^r dx P_F(x) S_F(x) \int_0^\infty dr' P_F(r')^2 v(r')
$$

$\longrightarrow$ consider ratio between exchange and correlation

$$
\frac{Q_{c\text{MP}^2}(r)}{Q_x(r)} = \frac{\int_0^\infty dr' K(r, r') v_{c\text{MP}^2}(r')}{\int_0^\infty dr' K(r, r') v_x(r')} \xrightarrow{r \to \infty} \frac{\int_0^\infty dr' P_F(r')^2 v_{c\text{MP}^2}(r')}{\int_0^\infty dr' P_F(r')^2 v_x(r')} = \text{const}
$$
Analysis of OPM equation for $r \to \infty$: Helium

Only Rydberg states included in $E_{c}^{\text{MP2}}$

\[ Q^a(r) \sim r P_N(r)^2 \times \text{const} \]
\[ Q^b(r) \sim P_N(r)^2 \times \text{const} \]

$P_N = \text{highest unoccupied state present in } E_{c}^{\text{MP2}}$
Analysis of OPM equation for \( r \to \infty \): Finite Hilbert space

Asymptotic form of orbitals (ordered with respect to eigenvalue): 
\[
P_{nl} \to A_{nl} r^{\beta_{nl}} e^{-\alpha_{nl} r}
\]

\[
\frac{P_{n-1,l}(r)}{P_{n,l}(r)} \xrightarrow{r \to \infty} 0 \quad \text{exponentially}
\]
Analysis of OPM equation for \( r \rightarrow \infty \): Finite Hilbert space

Asymptotic form of orbitals (ordered with respect to eigenvalue): 

\[ P_{nl} \rightarrow A_{nl} \, r^{\beta_{nl}} \, e^{-\alpha_{nl}r} \]

\[ \implies \frac{P_{n-1,l}(r)}{P_{n,l}(r)} \xrightarrow{r \rightarrow \infty} 0 \quad \text{exponentially} \]

Asymptotic behavior of ingredients of OPM equation under assumption \( v(r \rightarrow \infty) = 0 \)

\[ \int_{0}^{\infty} dr' \, K(r, r') \, v(r') \rightarrow C \, \frac{P_F(r)P_N(r)}{\epsilon_N - \epsilon_F} \int_{0}^{\infty} dr' \, P_F(r')P_N(r')v(r') \]

\[ Q^a(r) \rightarrow \frac{P_{N-1}(r)P_N(r)}{\epsilon_N - \epsilon_{N-1}} \int_{0}^{\infty} dr' \left[ P_{N-1}(r') \frac{\delta E}{\delta P_N(r')} - P_N(r') \frac{\delta E}{\delta P_{N-1}(r')} \right] \]

\[ Q^b(r) \rightarrow P_N(r)^2 \frac{\partial E}{\partial \epsilon_N} \]

with: \( P_F \) = highest occupied state, \( P_N \) = highest unoccupied state present in \( E \)

\[ \implies \text{different decay on left and right-hand side of OPM equation (} Q^a \text{ and } Q^b \text{ cannot cancel) } \]

\[ \implies \text{no solution as long as } E \text{ depends on unoccupied states} \]
Analysis of OPM equation for \( r \to \infty \): Rydberg states only

What if Hilbert space consists of "complete" set of Rydberg states?
Analysis of OPM equation for $r \to \infty$: Atom in box

What if complete spectrum is countable?

--- put atom in spherical box of radius $R_0 = 20$ Bohr (hard-wall boundary conditions)
Second order correlation potential: Atom in box

Helium in spherical box of radius $R_0 = 20$ Bohr

\( n_{\text{max}} = 300, \, \epsilon_{\text{max}} = 1100 \) Hartree, \( l = 0, 1, 2, \, I_{\text{max}} = 4800 \)

exact result from Umrigar, Gonze, PRA 50, 3827 (1994)
How to make the transition from discrete to continuum states?

Step 1: Choose large sphere of radius $R_0$, so that $P_{kl}(R_0)$ is close to asymptotic solution

$$\int_0^{R_0} dr \ P_{kl}^2(r) = \frac{2}{\pi} \int_0^{R_0} dr \ \sin[kr - \frac{\pi}{2} l - \eta_{kl}]^2 + \ldots = \frac{R_0}{\pi} + \ldots$$
How to make the transition from discrete to continuum states?

Step 1: Choose large sphere of radius $R_0$, so that $\overline{P}_{kl}(R_0)$ is close to asymptotic solution

$$\int_0^{R_0} dr \overline{P}_{kl}(r)^2 = \frac{2}{\pi} \int_0^{R_0} dr \sin[kr - \frac{\pi}{2} l - \eta_{kl}]^2 + \ldots = \frac{R_0}{\pi} + \ldots$$

Step 2: Discretize spectrum by requirement $P_{nl}(R_0) = 0$: $k_{nl}R_0 - \frac{\pi}{2} l - \eta_{nl} = n\pi$

$$\epsilon_{nl} = \frac{1}{2R_0^2} \left[ \left( n + \frac{l}{2} \right) \pi + \eta_{nl} \right]^2 \quad \implies \quad \frac{d\epsilon_{nl}}{dn} = \frac{\pi}{R_0} (2\epsilon_{nl})^{1/2} \quad \iff \quad \frac{dk_{nl}}{dn} = \frac{\pi}{R_0}$$
How to make the transition from discrete to continuum states?

Step 1: Choose large sphere of radius $R_0$, so that $\bar{P}_{kl}(R_0)$ is close to asymptotic solution

$$
\int_0^{R_0} dr \, \bar{P}_{kl}(r)^2 = \frac{2}{\pi} \int_0^{R_0} dr \, \sin[kr - \frac{\pi}{2} l - \eta_{kl}]^2 + \ldots = \frac{R_0}{\pi} + \ldots
$$

Step 2: Discretize spectrum by requirement $P_{nl}(R_0) = 0$: $k_{nl} R_0 - \frac{\pi}{2} l - \eta_{nl} = n\pi$

$$
\epsilon_{nl} = \frac{1}{2R_0^2} \left[ \left( n + \frac{l}{2} \right) \pi + \eta_{nl} \right]^2 \quad \Rightarrow \quad \frac{d\epsilon_{nl}}{dn} = \frac{\pi}{R_0} (2\epsilon_{nl})^{1/2} \quad \Leftrightarrow \quad \frac{dk_{nl}}{dn} = \frac{\pi}{R_0}
$$

Step 3: Renormalize positive energy states

$$
P_{nl}(r) \rightarrow \left( \frac{\pi}{R_0} \right)^{1/2} \bar{P}_{kl}(r)
$$

$$
\sum_n P_{nl}(r) P_{nl'}(r') \rightarrow \int_0^\infty dk \frac{dn}{dn} \frac{\pi}{R_0} \bar{P}_{kl}(r) \bar{P}_{kl'}(r') = \int_0^\infty dk \bar{P}_{kl}(r) \bar{P}_{kl'}(r')
$$

$\rightarrow$ continuum problem "recovered" in limit $R_0 \rightarrow \infty$
Continuum limit of OPM equation

Consider contribution of derivative with respect to positive energies

\[ Q^b = Q^b_- + Q^b_+ \]

\[
Q^b_+(r) = \frac{2}{R_0} \sum_l \int_0^\infty dk \overline{P}_{kl}(r)^2 \sum_{n_1 n_2 n_3} \frac{N(n_1 l_1, n_2 l_2 | n_3 l_3, kl)}{(\epsilon_{n_1 l_1} + \epsilon_{n_2 l_2} - \epsilon_{n_3 l_3} - \epsilon)^2} 
\]

\[
+ \frac{4}{R_0} \sum_{l l'} \int_0^\infty dk \overline{P}_{kl}(r)^2 \int_0^\infty dk' \sum_{n_1 n_2} \frac{N(n_1 l_1, n_2 l_2 | k l, k' l')}{(\epsilon_{n_1 l_1} + \epsilon_{n_2 l_2} - \epsilon - \epsilon')^2}
\]

\[ \rightarrow Q^b_+ \text{ vanishes in limit } R_0 \rightarrow \infty \quad (N(n_1 l_1, n_2 l_2 | n_3 l_3, \overline{kl}) \text{ and } Q^b_- \text{ remain finite}) \]
Consider contribution of derivative with respect to positive energies \( Q^b = Q^b_- + Q^b_+ \)

\[
Q^b_+(r) = \frac{2}{R_0} \sum_l \int_0^\infty dk \overline{P}_{kl}(r)^2 \sum_{n_1 n_2 n_3, l_1 l_2 l_3} \frac{N(n_1 l_1, n_2 l_2 | n_3 l_3, kl)}{(\epsilon_{n_1 l_1} + \epsilon_{n_2 l_2} - \epsilon_{n_3 l_3} - \epsilon)^2}
\]

\[+ \frac{4}{R_0} \sum_{ll'} \int_0^\infty dk \overline{P}_{kl}(r)^2 \int_0^\infty dk' \sum_{n_1 n_2, l_1 l_2} \frac{N(n_1 l_1, n_2 l_2 | kl, k'l')}{(\epsilon_{n_1 l_1} + \epsilon_{n_2 l_2} - \epsilon - \epsilon')^2}
\]

\( \rightarrow Q^b_+ \) vanishes in limit \( R_0 \rightarrow \infty \) \( (N(n_1 l_1, n_2 l_2 | n_3 l_3, kl) \) and \( Q^b_- \) remain finite\)

Finally reconsider sum rule

\[
\lim_{R_0 \rightarrow \infty} \int_0^{R_0} dr Q^b_+(r) \neq \int_0^\infty dr \lim_{R_0 \rightarrow \infty} Q^b_+(r) = 0
\]

\( \rightarrow \) OPM equation cannot be solved after continuum limit has been taken

Facco Bonetti et al., PRL 90, 219302 (2003)