# Big Picture and Background for Nuclear-Electronic Orbital (NEO) Approach: Calculating Mixed Nucleon-Electron Wave Functions

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Big Picture: What's a chemical interaction? Electrons, electrons... protons?

Specific Question: How to model relevant nucleon degrees of freedom

NEO is the ONE Random Phase Approximation (RPA) in the context of Density Functional Theory (DFT).

Method: How to solve the NEO Hamiltonian? Emergency crash-course in DFT Sketch of a derivation of RPA in DFT Outlook

# Chemistry is electron physics. The nucleus is cold and remote.

n-electrons in an external field (model):

$$\begin{aligned} \hat{H} &= \hat{T} + \hat{V}^{ee} + \hat{V}^{ext} \\ &= \sum_{i=1}^{n} T_i + \frac{1}{2} \sum_{i,j=1}^{n} \frac{1}{|r_i - r_j|} + \sum_{i=1}^{n} V^{ext}(r_i, r_c) \\ &= \sum_{i=1}^{n} T_i + \frac{1}{2} \sum_{i,j=1}^{n} \frac{1}{|r_i - r_j|} - \sum_{i=1}^{n} \frac{Z_A}{|r_i - r_Z|} \end{aligned}$$
(1)

What's left out? Extension to fully quantum treatment of Coulomb interaction (pre-Born-Oppenheimer):

$$\sum_{i}^{n+m} T_i + \frac{1}{2} \sum_{i,j}^{n} \frac{1}{|r_i - r_j|} - \sum_{Ai}^{n,m} \frac{Z_A}{|r_A - r_i|} + \sum_{AB}^{m} \frac{Z_A Z_B}{|r_A - r_B|}$$
(2)

# Chemistry is electron physics. The nucleus is cold and remote.

Schematic related to Born-Oppenheimer approximation from

J. Phys. Chem. Lett. 2018, 9, 17651770



Figure 2. Schematic depiction of the electron and proton excitations that can be computed with NEO-TDDFT in a single calculation. In the case shown, the electronic excitation energies are significantly greater than the proton vibrational excitation energies, leading to the separation depicted. For systems in which these excitation energies are similar (i.e., significant nonadiabatic or non-Born–Oppenheimer effects between the electrons and proton(s)), this separation would no longer be valid, and the single excitations would represent electron–proton vibronic excitations.

How much should we extend the model?

Atomic-nuclear fully-interacting system:

$$\hat{H}^{C,N} = \hat{T}_e + \hat{V}_{ee}^{C} + \hat{V}_{ep}^{C} + (\hat{T}_p + \hat{V}_{pp}^{C,N} + \hat{T}_n + \hat{V}_{nn}^{N} + \hat{V}_{np}^{N}) \quad (3)$$

- We don't care about nuclear (N) excitations - typically measured in MeV - for most chemical applications.

- So what *do* we want to model with Nuclear-Electronic Orbital (NEO) methods?

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# NEO is the ONE

"Nuclear quantum effects, such as zero point energy, nuclear tunneling, and vibrational excitations, play an important role in a wide range of chemical reactions."

- J. Chem. Phys. 117, 4106 (2002). {NEO-HF/CI/MCSCF paper}

- i.e. This will be most immediately useful for proton tunneling and similar special, but important, cases.

- NEO is the ONE (One Nucleon Extension\*) model:

$$\begin{aligned} \hat{H} &= \hat{T}_{e} + \hat{V}_{e}^{Z} + \hat{V}_{ee} \\ &+ \hat{T}_{p} + \hat{V}_{p}^{Z} + \hat{V}_{pp} + \hat{V}_{ep} \\ &\quad |\Psi^{e}\rangle \rightarrow |\Psi^{e,p}\rangle \end{aligned} \tag{4}$$

# NEO in action: J. Chem. Phys. 117, 4106 (2002). NEO-HF/CI/MCSCF paper

4116 J. Chem. Phys., Vol. 117, No. 9, 1 September 2002





FIG. 2. The two lowest energy NEO-HF hydrogen nuclear MO's for the transition state structure of malondehyde. Only the transferring hydrogen is treated quantum mechanically. The hydrogen nuclear MO is symmetric for the ground state (top) and antisymmetric for the first excited vibrational state (bottom). The orbitals are depicted as three-dimensional contour plots with a contour value of 0.01 bohr<sup>-3/2</sup>. The figure was generated with MAC MO. PLOT (RE-61).

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# NEO-RPA Project (present work)

Eva von Domaros' NEO-RPA project, with Oliver's help, is to:

- Derive a NEO-RPA energy functional theory, following "Electron correlation methods based on the random phase approximation" Theor Chem Acc (2012) 131:1084
- 2. Implement this theory within TURBOMOLE

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## Recent advances make RPA methods the attractive option

- RPA is a correction to HF, more cost effective than CI...
- Resolution of the identity approximation leads to O(N<sup>4</sup> log N) instead of O(N<sup>6</sup>) for RPA alone

 RPA calculations affordable for systems with over 100 atoms [Theor Chem Acc (2012) 131:1084]

## Emergency crash-course in DFT

Density Functional Theory (DFT) shifts interest from wave functions over 4n space-spin x = (r, σ) coordinates to particle densities over 4 coordinates:

$$\Psi(\vec{x_1}, \vec{x_2}, \dots, \vec{x_n}) \to \rho(\vec{x}) \tag{6}$$

The mapping is, in principle, invertible: wave functions and observables thereof can written as **functionals** of the density:

$$\Psi_0 = \Psi[\rho_0] \tag{7}$$

Typically, the ground state energy of the system - the objective - is found variationally/by minimizing:

$$E_0 = E[\rho_0] = \langle \Psi[\rho_0] | \hat{H} | \Psi[\rho_0] \rangle \tag{8}$$

## Sketch of a derivation of RPA in DFT

To use DFT, we can express the true ground state energy through an adiabatic connection to a simple mean-field approximation

$$E_{0}[\rho] = \langle \Psi[\rho] | \hat{H} | \Psi[\rho] \rangle + \langle \Phi_{0}[\rho] | \hat{H} | \Phi_{0}[\rho] \rangle - \langle \Phi_{0}[\rho] | \hat{H} | \Phi_{0}[\rho] \rangle$$
$$= \langle \Phi_{0}[\rho] | \hat{H} | \Phi_{0}[\rho] \rangle + E_{corr}[\rho]$$
$$= \langle \Phi_{0}[\rho] | \hat{H} | \Phi_{0}[\rho] \rangle + \int_{0}^{1} d\alpha W_{corr}^{\alpha}[\rho],$$
(9)

where,

$$\begin{aligned} \mathcal{H}^{\alpha} &= \mathcal{T} + \mathcal{V}^{\alpha}[\rho] + \alpha \mathcal{V}_{ee} + \mathcal{V}^{ext}; \\ \mathcal{H}^{\alpha=0} \left| \Phi_{0} \right\rangle = \epsilon_{0} \left| \Phi_{0} \right\rangle, \\ \hat{\mathcal{H}} &= \mathcal{H}^{\alpha=1}; \mathcal{V}^{\alpha=1} = 0. \end{aligned}$$
 (10)

## Sketch of a derivation of RPA in DFT

- ... we write things in terms of density fluctuations, then density-density response functions by the **fluctuation dissipation theorem**... 'cross-terms' with different phases cancel... "Random Phase Approximation"
- Eventually, we can derive an eigenvalue expression for  $E_{corr}^{RPA} = E_{corr}[\rho]$

### Outlook

#### Starting point

- Adiabatic connection Hamiltonian

$$\hat{H}^{\alpha} = \hat{H}^{\alpha,e} + \hat{H}^{\alpha,p} + \alpha \hat{V}^{ep}, \qquad (11)$$

 $\hat{H}^{\alpha,e/p}$  at  $\alpha = 0$  are interacting systems for just e/p. In contrast to J. Phys. Chem. Lett. 2018, 9, 1765-1770.

- Ground state energy functional

$$E_0[\rho^e, \rho^p] = \left\langle \Psi_0^{e,p}[\rho^e, \rho^p] \right| \hat{H}^{\alpha=1} \left| \Psi_0^{e,p}[\rho^e, \rho^p] \right\rangle + E_{corr}[\rho^e, \rho^p]$$
(12)

#### Outlook

#### Progress

We have (we think) the correlation energy  $E_{corr}$  in terms of a density-density response function:

$$E_{corr}^{ep} = -\int_0^1 d\alpha \int_0^\infty \frac{d\omega}{\pi} Im \int dx_e dx_p \frac{\chi^{\alpha, ep}(\omega, x_e, x_p)}{|r_e - r_p|}$$
(13)

The so-what:  $\chi$  is accessible from TDDFT, which has an alternate symplectic eigenvalue form [Theor Chem Acc (2012) 131:1084]. - RPA falls out as a zeroeth order approximation for  $\chi$ .

-Issue: 
$$\left\langle \Psi_{0}^{(0),ep} \middle| \Delta \rho_{e} \middle| \Psi_{n}^{(0),ep} \right\rangle = 0$$
 implies  $\chi^{(0),ep}$  is zero.

## Outlook

#### Next steps

The Dyson-type expression for the density-density response function is:

$$\chi^{\alpha} = \chi^{(0)} + \chi^{(0)} f^{\alpha}_{HXC} \chi^{\alpha}$$
  
=  $\chi^{(0)} + \chi^{(0)} f^{\alpha}_{HXC} \chi^{(0)} + \chi^{(0)} f^{\alpha}_{HXC} \chi^{(0)} f^{\alpha}_{HXC} \chi^{(0)} + \dots$  (14)