Excited States

McWeeny, “Methods of Molecular Quantum Mechanics” 2nd Ed
Chs.13&14

First Idea: CI

$$\begin{pmatrix} \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \end{pmatrix}\begin{pmatrix} \cdot \\ \cdot \\ \cdot \\ \cdot \end{pmatrix} = E_i \begin{pmatrix} \cdot \\ \cdot \\ \cdot \\ \cdot \end{pmatrix}$$

$$\mathbf{H} \quad \mathbf{c}_i = E_i \ \mathbf{c}_i$$

MCSCF, CISD, CIS, MR-CI, CASSCF, RASSCF

E_i <u>not</u> size consistent*

*except for CIS

$\Delta E_1 = E_i - E_0 \sim$ Intensive

<u>Linear Response:</u> Leveraging the Ground State

Suppose Ψ depends on some parameters, **p**, and determine Ψ_0 by:

$$\min E[\mathbf{p}] \equiv \langle \Psi[\mathbf{p}^*] | \hat{H} | \Psi[\mathbf{p}] \rangle \rightarrow |\Psi_0[\mathbf{p}]\rangle$$

$$\frac{dE}{dp^*} = \left\langle \frac{d\Psi_0}{dp^*} \right| \hat{H} \left| \Psi_0 \right\rangle = 0$$

Add a time dependent term to $\hat{H}$:

$$\hat{H}(t) = \hat{H} + \phi(t)\hat{A}$$

What will $\Psi(t)$ be?

$$\vec{p}(t) = \vec{p} + \vec{d}(t)$$

Time Dependent Variational Principle (TDVP)

$$\left\langle \frac{d\Psi(t)}{d\mathbf{p}^*} \middle| \hat{H}(t) - i\frac{\partial}{\partial t} \middle| \Psi(t) \right\rangle = 0$$

$$|\Psi(t)\rangle = |\Psi_0\rangle + \left|\frac{d\Psi_0}{d\vec{p}}\right\rangle \cdot \vec{d}(t) + \cdots$$

$$\left\langle \frac{d\Psi(t)}{d\vec{p}^*}\right| = \left\langle \frac{d\Psi_0}{d\vec{p}^*}\right| + \left\langle \frac{d^2\Psi_0}{d\vec{p}^* d\vec{p}^*}\right| \cdot \vec{d}(t) + \cdots$$

$$\left[\left\langle \frac{d\Psi_0}{d\vec{p}^*}\right| + \left\langle \frac{d^2\Psi_0}{d\vec{p}^* d\vec{p}^*}\right| \vec{d}(t)\right] \hat{H} - i\frac{\partial}{\partial t}\left[|\Psi_0\rangle + \left|\frac{d\Psi_0}{d\vec{p}}\right\rangle \cdot \vec{d}(t)\right] = 0$$

$\hookrightarrow$ free (not forced) oscillations

d-independent terms:

$$\left\langle \frac{d\Psi_0}{d\mathbf{p}^*} \middle| \hat{H} - i\frac{\partial}{\partial t} \middle| \Psi_0 \right\rangle = 0$$

true if I start in ground state

Terms linear in **d**:

$$\mathbf{d}^*(t)\left\langle \frac{d^2\Psi}{d\mathbf{p}^* d\mathbf{p}^*} \middle| \hat{H}(t) - i\frac{\partial}{\partial t} \middle| \Psi_0 \right\rangle + \left\langle \frac{d\Psi_0}{d\mathbf{p}^*} \middle| \hat{H}(t) - i\frac{\partial}{\partial t} \middle| \frac{d\Psi}{d\mathbf{p}} \right\rangle \mathbf{d}(t) = 0$$

All $H(t)$ $\downarrow$ H ! Sorry!

$$\Rightarrow \mathbf{d}^*(t)\left\langle \frac{d^2\Psi}{d\mathbf{p}^* d\mathbf{p}^*} \middle| \hat{H}(t) \middle| \Psi_0 \right\rangle + \left\langle \frac{d\Psi_0}{d\mathbf{p}^*} \middle| \hat{H}(t) \middle| \frac{d\Psi}{d\mathbf{p}} \right\rangle \mathbf{d}(t) = i\left\langle \frac{d\Psi_0}{d\mathbf{p}^*} \middle| \frac{d\Psi}{d\mathbf{p}} \right\rangle \dot{\mathbf{d}}(t)$$

Details response of system to fluctuations in $\vec{p}$!

$$\mathbf{A} \equiv \left\langle \frac{d\Psi_0}{d\mathbf{p}^*} \middle| \hat{H}(t) \middle| \frac{d\Psi}{d\mathbf{p}} \right\rangle \qquad \mathbf{B} \equiv \left\langle \frac{d^2\Psi}{d\mathbf{p}^* d\mathbf{p}^*} \middle| \hat{H}(t) \middle| \Psi_0 \right\rangle \qquad \mathbf{V} \equiv \left\langle \frac{d\Psi_0}{d\mathbf{p}^*} \middle| \frac{d\Psi}{d\mathbf{p}} \right\rangle$$

$$\underline{\underline{B}} \cdot \vec{d}^* + \underline{\underline{A}} \cdot \vec{d} = i \underline{\underline{V}} \cdot \dot{\vec{d}}$$

Now, we guess a form for $\mathbf{d}(t)$

$$\mathbf{d}(t) \equiv \mathbf{X}e^{-i\omega t} + \mathbf{Y}^* e^{i\omega t}$$

$$\Rightarrow \underline{\underline{B}} \cdot \left(\vec{X}^* e^{i\omega t} + \vec{Y} e^{-i\omega t} \right) + \underline{\underline{A}} \left(\vec{X} e^{-i\omega t} + \vec{Y}^* e^{i\omega t} \right)$$

$$= i \underline{\underline{V}} \left(-i\omega \vec{X} e^{-i\omega t} + i\omega \vec{Y}^* e^{i\omega t} \right)$$

$$e^{i\omega t}: \underline{\underline{B}} \cdot \vec{X}^* + \underline{\underline{A}} \cdot \vec{Y}^* = -\omega \underline{\underline{V}} \vec{Y}^* \xrightarrow{*} \underline{\underline{B}}^* \vec{X} + \underline{\underline{A}}^* \vec{Y} = -\omega \underline{\underline{V}} \vec{Y}$$

$$e^{-i\omega t}: \underline{\underline{B}} \cdot \vec{Y} + \underline{\underline{A}} \cdot \vec{X} = \omega \underline{\underline{V}} \vec{X}$$

Re-arrange:

$$\underset{H}{\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix}} \underset{C}{\begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}} = \underset{E}{\omega} \underset{S}{\begin{pmatrix} \mathbf{V} & 0 \\ 0 & -\mathbf{V} \end{pmatrix}} \underset{C}{\begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}}$$

$\omega = \Delta E_i$ (excitation energy)

Same derivation applies to any ***variational*** energy function:

$$E = \min_{\mathbf{p},\mathbf{q}} F\left[\langle \Psi[\mathbf{p}] |, | \Psi[\mathbf{q}] \rangle \right]$$

Examples:

LR-HF (aka TDHF, RPA)

$$\delta\phi_i(t)=\left(X_{ia}e^{-i\omega t}+Y_{ia}^{*}e^{-i\omega t}\right)\phi_a$$

$$\begin{pmatrix}\mathbf{A} & \mathbf{B}\\ \mathbf{B} & \mathbf{A}\end{pmatrix}\begin{pmatrix}\mathbf{X}\\ \mathbf{Y}\end{pmatrix}=\omega\begin{pmatrix}\mathbf{1} & 0\\ 0 & -\mathbf{1}\end{pmatrix}\begin{pmatrix}\mathbf{X}\\ \mathbf{Y}\end{pmatrix}$$

EOM-CC (LR-CC) not variational!

$$L[\ ] = E_{cc} - \lambda_{ij}^{ab}\langle\Phi_{ij}^{ab}|\bar{H}|\Phi_{HF}\rangle$$

LR-TD-DFT

$$\delta\phi_i(t)=\left(X_{ia}e^{-i\omega t}+Y_{ia}^{*}e^{-i\omega t}\right)\phi_a$$

Looks like TD-HF

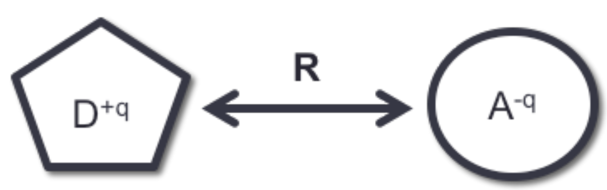
> **Theorem** (Runge-Gross) For a system that starts in the ground state and is subjected to a one-body potential v(**r**,t), there is a one-to-one correspondence between v(**r**,t) and ρ(**r**,t).

$\rho(t) \rightarrow$ Everything!

in Principle Exact.

Present TDDFT functionals have trouble with…

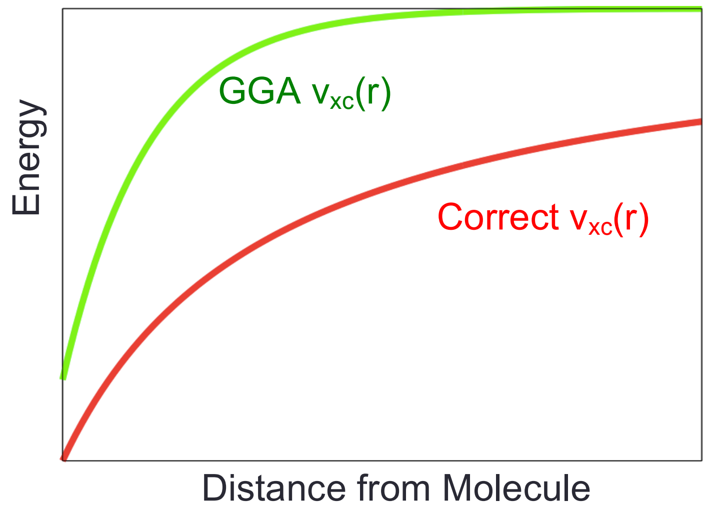
Charge Transfer Excited States



Source of problem: SIE (CT states come out too low)

Rydberg States

exist in continuum



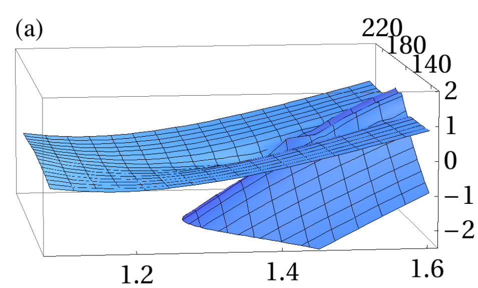
Double Excitations

$$\delta\phi_i(t) = \left(X_{ia}e^{-i\omega t} + Y_{ia}^{*}e^{-i\omega t}\right)\phi_a$$

Where are double excitations here?

Solution: $$\begin{pmatrix} \mathbf{A}(\omega) & \mathbf{B}(\omega) \\ \mathbf{B}(\omega) & \mathbf{A}(\omega) \end{pmatrix}\begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega\begin{pmatrix} \mathbf{1} & 0 \\ 0 & -\mathbf{1} \end{pmatrix}\begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}$$

Conical Intersections



Note: The conical intersection problem is a general "feature" of linear response methods. The ground state can never "know" that the excited state is there.

Suggested Further Reading: Dreuw and Head-Gordon, "Single Reference Methods for the calculation of excited states of large molecules", *Chem. Rev.* **105**, 4009-4037 (2005).