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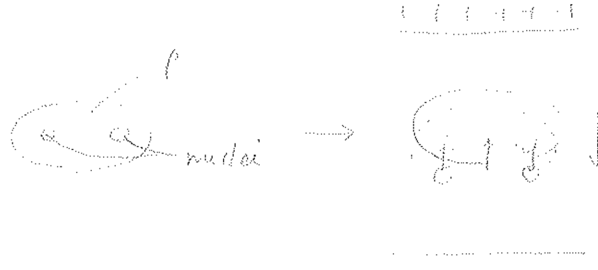
③ Response theory

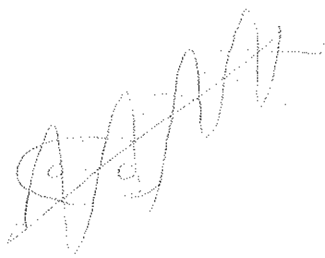


$\mu_{induced} = \alpha \mathcal{E} + \frac{1}{2}\beta \mathcal{E}^2 +$

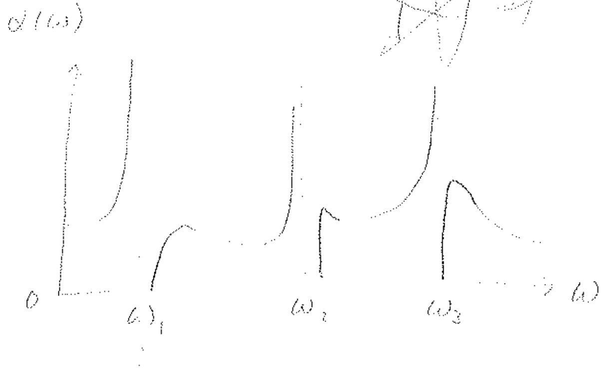
polarizability

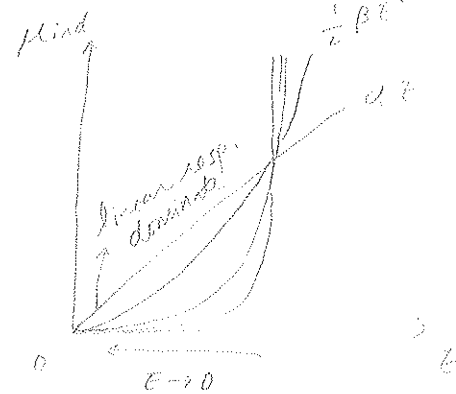
hyperpolarizability

electric field



$\mu_{induced} \cos\omega t = \alpha(\omega)\mathcal{E}\cos\omega t +$





finite response for infinitesimal perturbation $\equiv$ excitation

↳ i) detail of perturbation is irrelevant

ii) perturbation can be made to vanish at a later point in derivation

iii) linear response is exact for 1-photon excitation

④ Linear response theory   TDHF / TDDFT

Ⓘ $\sum_q \{ F_{pq\sigma} P_{qr\sigma} - P_{pq\sigma} F_{qr\sigma} \} = i \frac{\partial P_{pr\sigma}}{\partial t}$ time-dependent SCF

Ⓘⓘ $\sum_q P_{pq\sigma} P_{qr\sigma} = P_{pr\sigma}$ idempotency

Ⓘⓘⓘ $F_{pq\sigma} = H^{core}_{pq\sigma} + \sum_{rs} \sum_{\tau} P_{rs\tau} (p_\sigma q_\sigma || s_\tau r_\tau)$
$\qquad \sum_{rs} \sum_{\tau} P_{rs\tau} (p_\sigma q_\sigma | s_\tau r_\tau) + (p_\sigma | V_{xc}[P] | q_\sigma)$

Strategy

(i) Initial state = time-independent ground state satisfying Ⓘ (with RHS = 0) and Ⓘⓘ

(ii) Turn on (add to Ⓘⓘⓘ) time-dependent perturbation (= effect of photon) with freq ω

(iii) Expect time-dependent (also freq. ω) response in P and F (since F depends on P)

(iv) Collect terms that are linear in perturbation (1st order perturbation theory)

(i) Initial state

$P_{ij\sigma} = \delta_{ij}$, $P_{ia\sigma} = P_{ai\sigma} = P_{ab\sigma} = 0$ $\begin{pmatrix} \mathbb{1} & 0 \\ 0 & 0 \end{pmatrix}$

$F_{pq\sigma} = \delta_{pq} \epsilon_{p\sigma}$ $\begin{pmatrix} \epsilon_1 & & \\ & \ddots & \\ & & \epsilon_n \end{pmatrix}$

(Obviously they satisfy
$\mathbb{F}\mathbb{P} - \mathbb{P}\mathbb{F} = 0$
$\mathbb{P}\mathbb{P} = \mathbb{P}$)

(ii) $F_{pq\sigma}{}' = F_{pq\sigma} + \underbrace{\frac{1}{2} \{ g_{pq\sigma} e^{-i\omega t} + g^*_{pq\sigma} e^{i\omega t} \}}_{G_{pq\sigma}}$ c.c. (Hermitian)   ("$\frac{1}{2}$" and "g" details unimportant)

(iii) $P_{pq\sigma}{}' = P_{pq\sigma} + \underbrace{\frac{1}{2} \{ d_{pq\sigma} e^{-i\omega t} + d^*_{pq\sigma} e^{i\omega t} \}}_{D_{pq\sigma}}$

$F_{pq\sigma}{}'' = F_{pq\sigma}{}' + \underbrace{\sum_{rs\tau} \frac{\partial F_{pq\sigma}}{\partial P_{rs\tau}} D_{rs\tau}}_{\text{first order}} + \underbrace{\cdots}_{\text{second and higher order}}$

$$\frac{\partial F_{pq\sigma}}{\partial P_{rs\tau}} = \frac{\partial\left\{\sum_{rs}\sum_{\tau} P_{rs\tau}\,(p_\sigma q_\sigma|s_\tau r_\tau) + (p_\sigma|V_{xc}|q_\sigma)\right\}}{\partial P_{rs\tau}}$$

(DFT case; HF $(\cdot|\cdot) \to (\cdot||\cdot)$ and lose V_{xc} term)

$$= (p_\sigma q_\sigma|s_\tau r_\tau) + \Big(p_\sigma^{1^*}\Big|\underbrace{\frac{\partial\rho(2)}{\partial P_{rs\tau}}}_{\varphi_{r\tau}(2)\varphi^*_{s\tau}(2)}\frac{\delta V_{xc}^{(1)}}{\delta\rho(2)}\Big|q_\sigma^{1}\Big)$$

$$= (p_\sigma q_\sigma|s_\tau r_\tau) + \Big(p_\sigma^{1^*} q_\sigma^{1}\Big|\underbrace{\frac{\delta^2 f}{\delta\rho(1)\delta\rho(2)}}_{xc\ \text{kernel}}\Big|s_\tau^{2^*} r_\tau^{2}\Big) \equiv (p_\sigma q_\sigma||s_\tau r_\tau)$$

(IV) Schematically from $FP - PF = i\frac{\partial}{\partial t}P$

$$\left(F + \underset{\sim}{G} + \frac{\partial F}{\partial P}\underset{\sim}{D}\right)\left(P + \underset{\sim}{D}\right) - \left(P + \underset{\sim}{D}\right)\left(F + \underset{\sim}{G} + \frac{\partial F}{\partial P}\underset{\sim}{D}\right) = i\frac{\partial}{\partial t}(P + \underset{\sim}{D}) \rightsquigarrow \text{first order response}$$

$$FD - DF + \left(G + \frac{\partial F}{\partial P}D\right)P - P\left(G + \frac{\partial F}{\partial P}D\right) = i\frac{\partial}{\partial t}D$$

Specifically, collecting those terms $\propto e^{-i\omega t}$, ($e^{i\omega t}$ terms lead to c.c.)

$$\sum_{q}\Big[(F_{pq\sigma}d_{qr\sigma} - d_{pq\sigma}F_{qr\sigma}) + \Big(g_{pq\sigma} + \sum_{t,s,\tau}(p_\sigma q_\sigma||t_\tau s_\tau)d_{st\tau}\Big)P_{qr\sigma}$$
$$- P_{pq\sigma}\Big(g_{qr\sigma} + \sum_{t,s,\tau}(q_\sigma r_\sigma||t_\tau s_\tau)d_{st\tau}\Big)\Big] = \underbrace{\omega}_{\text{comes from } i\frac{\partial}{\partial t}e^{-i\omega t}} d_{pr\sigma}$$

Schematically from $PP = P$

$$(P + \underset{\sim}{D})(P + \underset{\sim}{D}) = P + \underset{\sim}{D}$$

$$PD + DP = D$$

$$PDP + \underbrace{DP^2}_{=DP} = DP \rightarrow PDP = 0$$

$$\Big(\sum_{i,j} P_{ii}D_{ij}P_{jj} = 0\Big) \quad D_{ij} = 0$$

$$PD = D - DP = D(1-P)$$

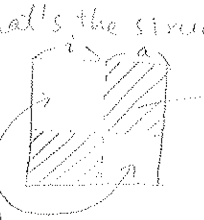
$$(1-P)PD = (1-P)D(1-P)$$

$$(1-P)PD = (P - P^2)D = 0$$

$$\longrightarrow (1-P)D(1-P) = 0$$

$$D_{ab} = 0$$

What's the structure of D?



mixing of occ. with virt.

rotation among occ. only or virt. only

they donot contribute!

$\det U^\dagger A U = \det U^\dagger \cdot \det U \det A = \det U^\dagger U \det A = \det A$

$$P = \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} \quad \text{Projector on occ.}$$

$$1 - P = \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix} \quad \text{Projector on virt.}$$

Only D_{ia} and D_{ai} are meaningful!

rename $d_{ai\sigma} = x_{ai\sigma}$, $d_{ia\sigma} = y_{ai\sigma}$ and use $F_{pq\sigma} = \epsilon_{p\sigma}\delta_{pq}$ and $P_{ii\sigma} = 1$ (else 0)

$$(\epsilon_a - \epsilon_i) x_{ai\sigma} + g_{ai\sigma} + \sum_{b,j,\tau} (a_\sigma i_\sigma ||| j_\tau b_\tau) x_{bj\tau} + \sum_{b,j,\tau} (a_\sigma i_\sigma ||| b_\tau j_\tau) y_{bj\tau} = \omega x_{ai\sigma}$$

$$(\epsilon_i - \epsilon_a) y_{ai\sigma} - g_{ia\sigma} + \sum_{b,j,\tau} (i_\sigma a_\sigma ||| j_\tau b_\tau) x_{bj\tau} + \sum_{b,j,\tau} (i_\sigma a_\sigma ||| b_\tau j_\tau) y_{bj\tau} = \omega y_{ai\sigma}$$

$$\text{IV} \quad \begin{pmatrix} \mathbb{A} & \mathbb{B} \\ \mathbb{B}^* & \mathbb{A}^* \end{pmatrix} \begin{pmatrix} \mathbb{X} \\ \mathbb{Y} \end{pmatrix} = \omega \begin{pmatrix} \mathbb{1} & \mathbb{0} \\ \mathbb{0} & -\mathbb{1} \end{pmatrix} \begin{pmatrix} \mathbb{X} \\ \mathbb{Y} \end{pmatrix} - \begin{pmatrix} \mathbb{g} \\ \mathbb{g}^* \end{pmatrix}$$

$$A_{ai\sigma, bj\tau} = \delta_{ij}\delta_{ab}\delta_{\sigma\tau}(\epsilon_a - \epsilon_i) + (a_\sigma i_\sigma ||| j_\tau b_\tau)$$

HF: $(a_\sigma i_\sigma | j_\tau b_\tau) - (a_\sigma b_\tau | j_\tau i_\sigma)$

DFT: $(a_\sigma i_\sigma | j_\tau b_\tau) + (a_\sigma i_\sigma | \frac{\delta f}{\delta\rho_\sigma \delta\rho_\tau} | j_\tau b_\tau)$

$$B_{ai\sigma, bj\tau} = (a_\sigma i_\sigma ||| b_\tau j_\tau)$$

a) When $\mathbb{g} = 0$, IV is a non Hermitian eigenvalue eq. ω is an excitation energy. TDHF, TDDFT

b) When $\mathbb{g}$ is a dipole integral matrix, IV is a ω-dependent set of linear eqs. $(\mathbb{g} \cdot \mathbb{X} + \mathbb{g}^* \mathbb{Y})$ is a freq.-dependent polarizability

c) When $\mathbb{g}$ is a geometrical derivative of Fock / KS Hamiltonian matrix, $\mathbb{X}$ and $\mathbb{Y}$ are response of MO's to the geometrical perturbation necessary in HF, KS analytical second derivatives. Eq is called CPHF, CPKS.

d) When $\mathbb{g} = 0$, $^\forall \omega < 0$, the initial state is not the ground state. HF, KS DFT stability analysis.

(e) When $\mathbb{g}$ is a dipole, ω is imaginary, $(\mathbb{g} \cdot \mathbb{X} + \mathbb{g}^* \cdot \mathbb{Y})$ are integrated to yield van der Waals C_6 coefficients)

⑤ Algorithms

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

DFT case

$$A_{ai\sigma,bj\tau} = \delta_{ij}\delta_{ab}\delta_{\sigma\tau}(\epsilon_{a\sigma} - \epsilon_{i\sigma}) + (a_\sigma i_\sigma | j_\tau b_\tau) + (a_\sigma i_\sigma | \frac{\delta^2 E_{xc}}{\delta\rho\,\delta\rho} | j_\tau b_\tau)$$

$$B_{ai\sigma,bj\tau} = (a_\sigma i_\sigma | b_\tau j_\tau) + (a_\sigma i_\sigma | \frac{\delta^2 E_{xc}}{\delta\rho\,\delta\rho} | b_\tau j_\tau)$$

same if orbitals are real and no hybrid ($-(ab|ji)$ appear)
$-(aj|bi)$

i) Tamm-Dancoff $B=0$. TDHF $\to$ CIS, TDDFT $\to$ Tamm-Dancoff TDDFT

$$AX = \omega X$$

ii) Assume real orbitals

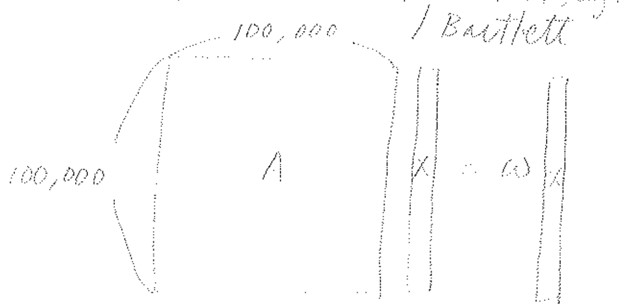
$$AX + BY = \omega X$$
$$\pm)\ BX + AY = -\omega Y$$

$$(A+B)(X+Y) = \omega(X-Y)$$
$$(A-B)(X-Y) = \omega(X+Y)$$

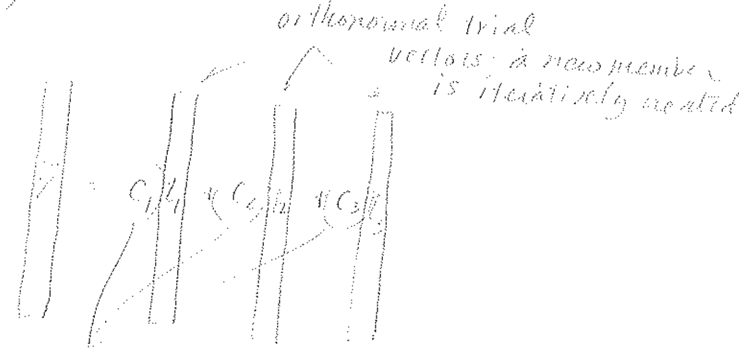
$$(A-B)(A+B)(X+Y) = \omega(A-B)(X-Y) = \omega^2(X+Y)$$

$$\underbrace{(A-B)}_{\substack{(\epsilon_{a\sigma} - \epsilon_{i\sigma}) \\ \text{(for pure DFT)}}}(A+B)(X+Y) = \omega^2(X+Y)$$

iii) Trial vector - subspace diagonalization method for large matrices
(Davidson / Nakatsuji-Hirao / Bartlett)



only for a few lowest roots



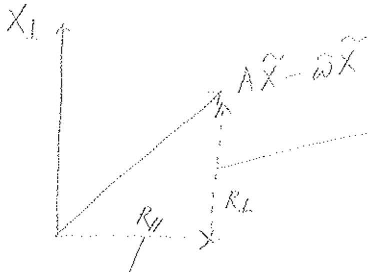
variationally determined to minimize $\langle \tilde{X} | A\tilde{X} - \omega\tilde{X} \rangle$

full diagonalization
$O(n^3)$

subspace diag.
$O(n^2 n_l)$

$$\frac{n_l}{n} = \frac{3}{100{,}000}$$

$$\tilde{X} = \sum_{i=1}^{m} c_i t_i$$



perpendicular component is used as the seed for the new vector $\to \tilde{X}$

parallel component is minimized by adjusting $\{c\}$

$$|R_\parallel| = \langle \hat{X} | A\hat{X} - \tilde{\omega}\hat{X} \rangle$$

$$= \sum_{i,j} c_i c_j \langle t_i | A | t_j \rangle - \hat{\omega} \sum_{i,j} c_i c_j \delta_{ij}$$

$$0 = \frac{\partial}{\partial c_i} |R_\parallel| = 2\sum_j \langle t_i | A | t_j \rangle c_j - 2\hat{\omega} c_i$$

$$\tilde{A} c = \hat{\omega} c$$

Also linear eq.
→ Pople / CPHF
→ Pulay / DIIS

if $|R_\perp| >$ threshold (typically 10^{-6}), $(R_\perp)_i = (R_\perp)_i / A_{ii}$

$R_\perp$ is Schmidt orthogonalized with t_1, t_i, t_m

normalized and added to $\{t\}$ as t_{m+1}

iv) $\dfrac{\delta^2 E_{xc}}{\delta\rho\,\delta\rho}$ exchange correlation kernel

$$E_{xc} = \int f[\overbrace{\rho_\alpha, \rho_\beta}^{LDA}, \overbrace{\gamma_{\alpha\alpha}, \gamma_{\alpha\beta}, \gamma_{\beta\beta}}^{GGA}]\, d1$$

$\gamma_{\alpha\alpha} = \nabla\rho_\alpha \cdot \nabla\rho_\alpha$
$\gamma_{\alpha\beta} = \nabla\rho_\alpha \cdot \nabla\rho_\beta$

$$(p_\alpha | V_{xc} | q_\alpha) = \int \Big(\underbrace{\frac{\partial f}{\partial \rho_\alpha} \varphi_{p\alpha}\varphi_{q\alpha}}_{(a)} + \underbrace{2\frac{\partial f}{\partial \gamma_{\alpha\alpha}} \nabla\rho_\alpha \cdot \nabla(\varphi_{p\alpha}\varphi_{q\alpha})}_{(b)} + \underbrace{\frac{\partial f}{\partial \gamma_{\alpha\beta}} \nabla\rho_\beta \cdot \nabla(\varphi_{p\alpha}\varphi_{q\alpha})}_{(c)} \Big) d1$$

similarly for $(p_\beta | V_{xc} | q_\beta)$

$$
\begin{aligned}
\left(i_\alpha a_\alpha \left| \frac{\delta^2 E_{xc}}{\delta\rho_\alpha \delta\rho_\alpha} \right| j_\alpha b_\alpha\right) &= \int (\psi_{i\alpha}\psi_{a\alpha}) \frac{\partial^2 f}{\partial^2 \rho_\alpha} (\psi_{j\alpha} \psi_{b\alpha})\, d1 && \frac{\partial (a)}{\partial \rho_\alpha} \\
&+ 2\int (\psi_{i\alpha}\psi_{a\alpha}) \frac{\partial^2 f}{\partial\rho_\alpha \partial\gamma_{\alpha\alpha}} \nabla\rho_\alpha \cdot \nabla(\psi_{j\alpha}\psi_{b\alpha})\, d1 && \frac{\partial (b)}{\partial \rho_\alpha} \\
&+ 2\int (\psi_{j\alpha}\psi_{b\alpha}) \frac{\partial^2 f}{\partial\rho_\alpha \partial\gamma_{\alpha\alpha}} \nabla\rho_\alpha \cdot \nabla(\psi_{i\alpha}\psi_{a\alpha})\, d1 && \frac{\partial (a)}{\partial \gamma_{\alpha\alpha}} \\
&+ 2\int \nabla(\psi_{i\alpha}\psi_{a\alpha}) \cdot \nabla(\psi_{j\alpha}\psi_{b\alpha}) \frac{\partial f}{\partial\gamma_{\alpha\alpha}}\, d1 && \frac{\partial (b)}{\partial \rho_\alpha} \quad \left(\frac{\partial \nabla\rho_\alpha}{\partial\rho_\alpha}\right) \\
&+ \int (\psi_{i\alpha}\psi_{a\alpha}) \frac{\partial^2 f}{\partial\rho_\alpha \partial\gamma_{\alpha\beta}} \nabla\rho_\beta \cdot \nabla(\psi_{j\alpha}\psi_{b\alpha})\, d1 && \frac{\partial (c)}{\partial \rho_\alpha} \\
&+ \int (\psi_{j\alpha}\psi_{b\alpha}) \frac{\partial^2 f}{\partial\rho_\alpha \partial\gamma_{\alpha\beta}} \nabla\rho_\beta \cdot \nabla(\psi_{i\alpha}\psi_{a\alpha})\, d1 && \frac{\partial (a)}{\partial \gamma_{\alpha\alpha}} \\
&+ 4\int \nabla\rho_\alpha \cdot \nabla(\psi_{i\alpha}\psi_{a\alpha}) \frac{\partial^2 f}{\partial\gamma_{\alpha\alpha}^2} \nabla\rho_\alpha \cdot \nabla(\psi_{j\alpha}\psi_{b\alpha})\, d1 && \frac{\partial (b)}{\partial \gamma_{\alpha\alpha}} \\
&+ 2\int \nabla\rho_\alpha \cdot \nabla(\psi_{i\alpha}\psi_{a\alpha}) \frac{\partial^2 f}{\partial\gamma_{\alpha\alpha}\partial\gamma_{\alpha\beta}} \nabla\rho_\beta \cdot \nabla(\psi_{j\alpha}\psi_{b\alpha})\, d1 && \frac{\partial (c)}{\partial \gamma_{\alpha\alpha}} \\
&+ 2\int \nabla\rho_\alpha \cdot \nabla(\psi_{j\alpha}\psi_{b\alpha}) \frac{\partial^2 f}{\partial\gamma_{\alpha\alpha}\partial\gamma_{\alpha\beta}} \nabla\rho_\beta \cdot \nabla(\psi_{i\alpha}\psi_{a\alpha})\, d1 && \frac{\partial (b)}{\partial \gamma_{\alpha\beta}} \\
&+ \int \nabla\rho_\beta \cdot \nabla(\psi_{i\alpha}\psi_{a\alpha}) \frac{\partial^2 f}{\partial\gamma_{\alpha\beta}^2} \nabla\rho_\beta \cdot \nabla(\psi_{j\alpha}\psi_{b\alpha})\, d1 && \frac{\partial (c)}{\partial \gamma_{\alpha\beta}}
\end{aligned}
$$

Similarly for $\left(i_\alpha a_\alpha \left| \frac{\partial^2 E_{xc}}{\delta\rho_\alpha \delta\rho_\beta} \right| j_\beta b_\beta\right)$

v) AO-based algorithm

$$
\sum_{b,j} \underbrace{(\overset{\text{MO's}}{a_\sigma i_\sigma} \,|||\, \overset{\text{MO's}}{j_\tau b_\tau})}_{\sum_{\substack{\mu,\nu\\ \kappa,\lambda}} \underbrace{C^\mu_{a\sigma} C^\nu_{i\sigma} C^\kappa_{j\tau} C^\lambda_{b\tau}}_{\text{MO coefficients}} \underbrace{(\mu\nu|||\kappa\lambda)}_{\text{AO}}} x_{bj\tau} = \sum_{\mu\nu} C^\mu_{a\sigma} C^\nu_{i\sigma} \underbrace{\sum_{\kappa\lambda} (\mu\nu|||\kappa\lambda) \underbrace{\sum_{b,j} C^\kappa_{j\tau} C^\lambda_{b\tau} x_{bj\tau}}_{\substack{\text{step 1} \quad O(n^3)\\ x_{\kappa\lambda\tau}}}}_{\substack{\text{step 2} \quad O(n^4)\\ z_{\mu\nu\tau}}}
$$

$O(n^5)$

$\downarrow$

AO's

MO's

step 3 final $O(n^3)$

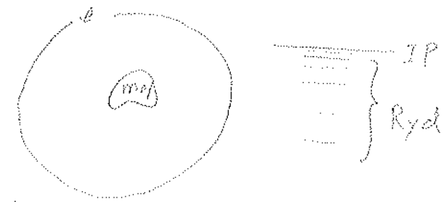
ⓑ Performance (TDDFT)

i) Scaling — basically the same as DFT for the ground state

ii) Valence excited states — 0.3 eV
(closed/open shells)

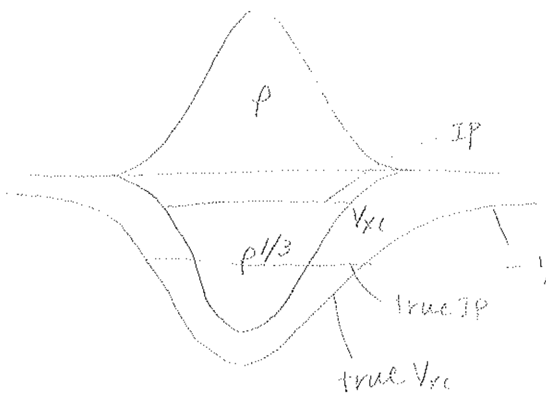
Rydberg excited states — poor (too low)

IP — poor (too small)



Coulomb — exchange

$(ii|ii) - (ii|ii)$



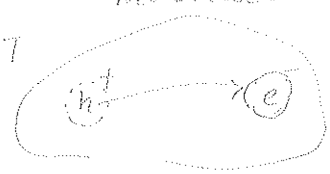
1/r (self interaction tail)

Polarizability — too large $\left(\alpha_{xy} \sim \dfrac{\langle \Phi|\hat{x}|\Phi_i^a\rangle\langle\Phi_i^a|\hat{y}|\Phi\rangle}{\underbrace{\varepsilon_i^a - \varepsilon_0}_{\text{too small}}}\right)$

vdW C_6 — too large

CT — too small

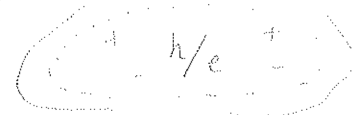
true CT



$\underbrace{(ii|ii)}_{\text{Coulomb}}$ — $\underset{\text{insufficient cancellation}}{XC}$

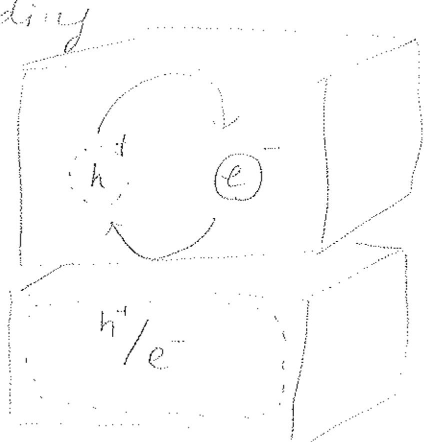
large if φ_i is localized ... small if φ_i is delocalized

(TD)DFT prefers delocalized picture



exciton (in solids) — no binding
(no large systems!)

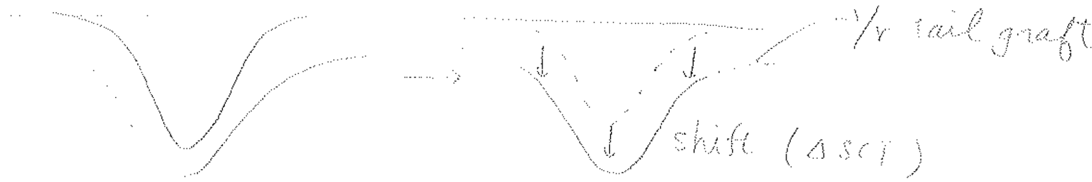
true exciton



(TD)DFT
hole/electron completely delocalized

iii) Some fixes

ⓐ Asymptotic correction (fixes Rydberg, IP, vdW C_6)



ⓑ Range separated (fixes CT, probably exciton)

$$
(a_\sigma i_\sigma ||| j_\tau b_\tau) = \begin{cases} \overbrace{(a_\sigma i_\sigma | j_\tau b_\tau) + \left(a_\sigma i_\sigma \middle| \dfrac{\delta^2 E_{xc}}{\delta\rho\,\delta\rho} \middle| j_\tau b_\tau\right)}^{\text{DFT-type}} & \text{distance } (ai-jb) \le r_0 \\ \underbrace{(a_\sigma i_\sigma | j_\tau b_\tau) - (a_\sigma b_\tau | j_\tau i_\sigma)}_{\text{HF type}} & \text{distance } (ai-jb) > r_0 \end{cases}
$$

① Early history

1996 Jamorski, Casida, Salahub, JCP 104 5134

1996,7 Bauernschmitt, Häser, Treutler, Ahlrichs, CPL 256, 454; 264, 573

1998 Stratmann, Scuseria, Frisch, JCP 109, 8218

1999 Hirata, Head-Gordon CPL 302, 375; 314, 291

IP, Rydberg, polarizability problems

1998 Casida et al. JCP 108, 4439

1998 Tozer, Handy, JCP 109, 10180

CT problems

2003 Dreuw, Weisman, Head-Gordon, JCP 119, 2943

Range-separated

2001 Iikura, Tsuneda, Yanai, Hirao, JCP 115 3540

2005 Kamiya, Sekino, Tsuneda, Hirao, JCP 122 234111

vdW

1995 van Gisbergen, Snijders, Baerends, JCP 103 9347

2002 Kamiya, Tsuneda, Hirao, JCP 117, 6010 (range separated)

Review

2005 Dreuw, Head-Gordon CR 105, 4009

Extended systems

1999 Hirata, Head-Gordon, Bartlett, JCP 111, 10774

Analytical gradients

1999 Van Caillie, Amos CPL, 308, 249