Making GW, RPA and beyond work with localized orbitals

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State-of-the-art first-principles methods

- Ground-state energy

Density-functioinal theory with advanced exchange-correlation energy functional: hybrid functionals, random-phase approximation (RPA), and beyond

$$E_{xc} = E_{xc}[\epsilon_n, \psi_n]$$

- Single-particle excitation energy (self-energy!)

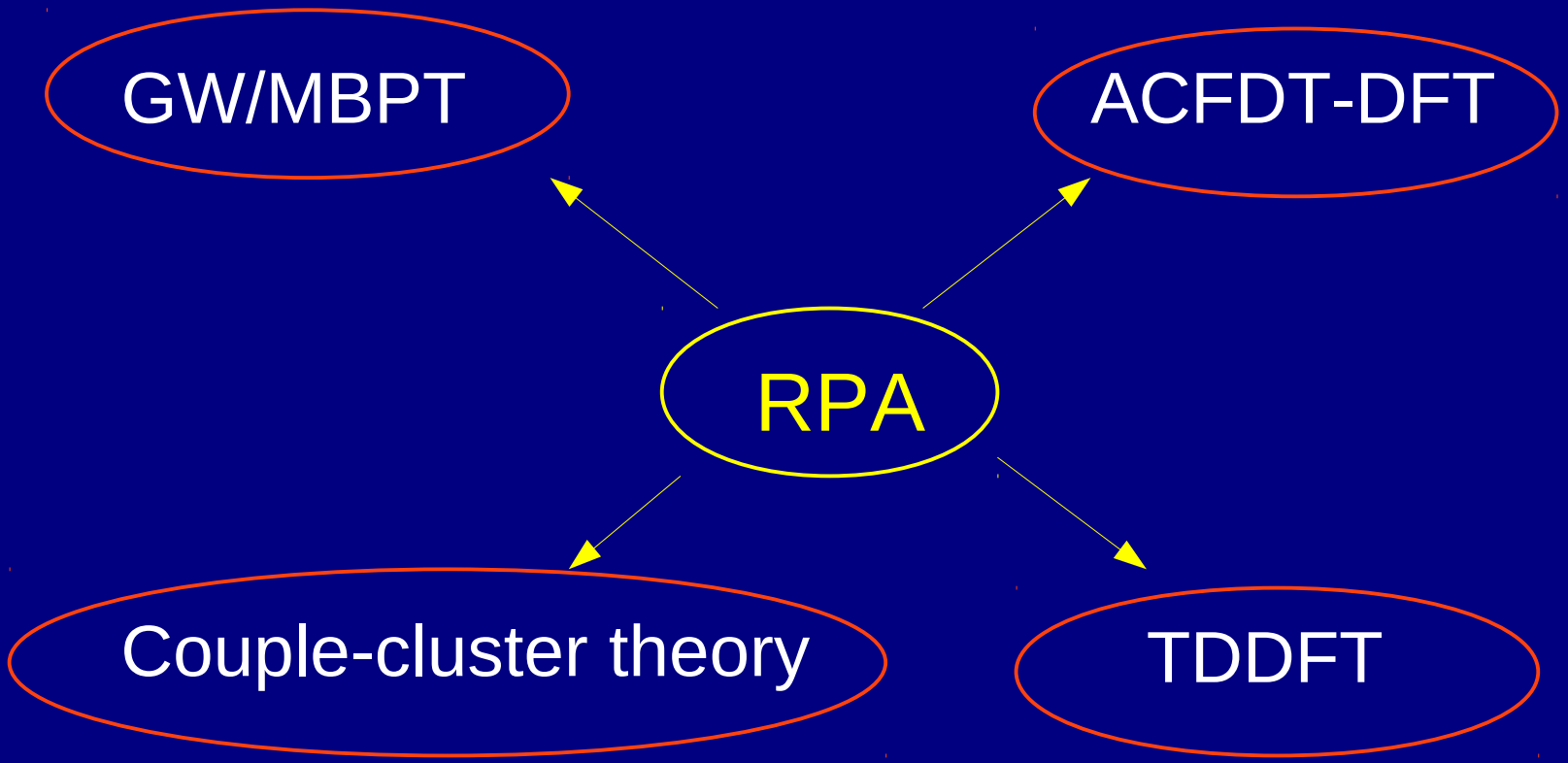
$$\epsilon_s = E(N,0) - E(N-1,s); \quad \epsilon_t = E(N+1,t) - E(N,0)$$

The *GW* approximation

- Optical excitations (creation of particle-hole pairs)

$$E_s = E(N,0) - E(N,s)$$

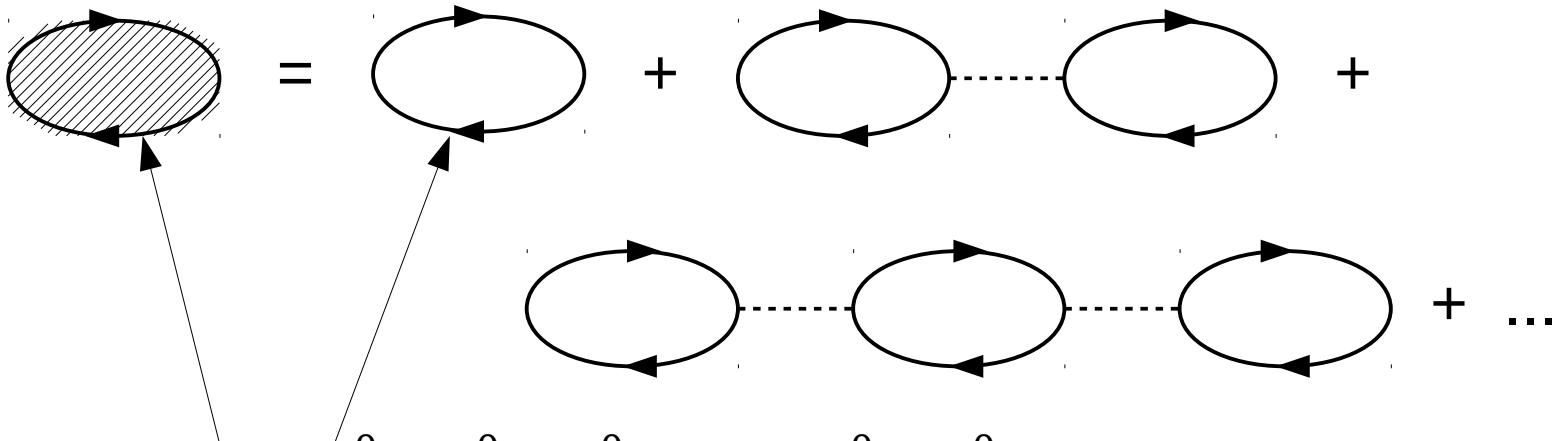
Bethe-Salpeter Equation, TDDFT


GW/MBPT
ACFDT-DFT
RPA
Couple-cluster theory
TDDFT

Early history of RPA

- Correlation energy of homogeneous electron gas (HES):
  Divergence disaster of "order-by-order" perturbation theory
- Separation of collective modes and quasiparticle modes:
  First appearance of the RPA concept (Bohm & Pines, 1950)
- Self-consistent field approach to HES
  Lindhard function (Lindhard, 1954)
- RPA = "sum of ring diagrams to infinite order"
  (Brueckner & Gell-Mann, 1957)
- The concept of screened Coulomb interaction W
  (Hubbard, 1957)
- The GW approximation $\Sigma = iGW$ (Hedin, 1965)

RPA and the Lindhard function



$$\chi \approx \chi^0 + \chi^0 v \chi^0 + \cdots = \chi^0 + \chi^0 v \chi$$

Lindhard function:

$$\chi_0(\boldsymbol{k},\omega) = 2 \int_{\substack{q<k_F \\ k+q>k_F}} \left[\frac{1}{\omega + i\eta - \epsilon_{\boldsymbol{k}+\boldsymbol{q}} + \epsilon_{\boldsymbol{q}}} - \frac{1}{\omega - i\eta + \epsilon_{\boldsymbol{k}+\boldsymbol{q}} + \epsilon_{\boldsymbol{q}}} \right]$$

$$\epsilon_k = k^2/2\mathrm{m}$$

M. Gell-Mann and K. A. Brueckner, Phys. Rev. **106**, 364 (1957)

Correlation energy of HES

$$E_c^{\mathrm{RPA}} = -\frac{1}{2}\int_0^1 d\lambda \int_0^\infty \frac{d\omega}{2\pi}\int \frac{d^3k}{(2\pi)^3}\sum_{n=2}^{\infty}\left[\lambda v \chi^0(\boldsymbol{k}, i\omega)\right]^n$$

$$= \frac{1}{(2\pi)^4}\int_0^\infty d\omega \int d^3k \left[\ln(1-\chi^0 v)+\chi^0 v\right]$$

Bohr radius

$$\frac{4\pi}{3} r_s^3 a_0^3 = 1/n$$

Electron density

Second-order exchange

$$E_0(r_s) = \frac{2.21}{r_s^2} - \frac{0.916}{r_s} - 0.096 + 0.062\ln(r_s) + \cdots \quad [Ryd]$$

Kinetic energy

Exchange energy

The RPA correlation

Influence of the RPA concept

- Plasmon excitations
- Friedel oscilation (3D metals)
- Kohn anomaly (electron-phonon coupling)
- Peierls instability (dimerization of 1D atomic chains)
- Itinerant ferromagnetism (Stoner's model)
- Nuclear physics

……

RPA as a first principles method

- With the framework of adiabatic-connection fluctuation-dissipation theorem, RPA can be formualted as an approximate, but fully nonlocal exchange-correlation energy functional, sitting at the fifth-rung of Jacob's ladder (according to Perdew's classification) .

  Langreth & Perdew, Phys. Rev. B 15, 2884 (1997).
  Gunnarsson & Lundqvist, Phys. Rev. B 13, 4274 (1976)

- First application to real molecules

  Furche, Phys. Rev. B 64, 195120 (2001)

- Widespread applications to molecules, solids, surfaces, and layered materials (2001-present)

Basic formalism

Kohn-Sham eigenvalues and eigenfunctions:

$$\epsilon_n, \psi_n$$

Independent-particle response function:

$$\chi^0(\boldsymbol{r},\boldsymbol{r}',i\omega)=\sum_{m,n}\frac{(f_m-f_n)\psi_m^*(\boldsymbol{r})\psi_n(\boldsymbol{r})\psi_n^*(\boldsymbol{r}')\psi_m(\boldsymbol{r}')}{\epsilon_m-\epsilon_n-i\omega}$$

RPA

$$E_c^{\mathrm{RPA}}=\frac{1}{2\pi}\int_0^\infty d\omega\,\mathrm{Tr}\left[\ln(1-\chi_0 v)+\chi_0 v\right]$$

G_0W_0

$$W_0(i\omega)=v/[1-\chi_0(i\omega)v]$$

$$\Sigma^{GW}(i\omega)=\frac{i}{2\pi}\int d\omega' G_0(i\omega-i\omega')W_0(i\omega')$$

Basic formalism

Kohn-Sham eigenvalues and eigenfunctions:

$$\epsilon_n, \psi_n$$

Independent-particle response function:

$$\chi^0(\boldsymbol{r},\boldsymbol{r}',i\omega)=2\sum_{mn}\frac{(f_m-f_n)\psi_m^*(\boldsymbol{r})\varphi_n(\boldsymbol{r})\varphi_n^*(\boldsymbol{r}')\varphi_m(\boldsymbol{r}')}{\epsilon_m-\epsilon_n-i\omega}$$

RPA

$$E_c^{\mathrm{RPA}}=\frac{1}{2\pi}\int_0^\infty d\omega\,\mathrm{Tr}\left[\ln(1-\chi^0 v)+\chi^0 v\right]$$

G_0W_0

$$W_0(i\omega)=v/[1-\chi^0(i\omega)v]$$

$$\Sigma^{GW}(i\omega)=\frac{i}{2\pi}\int d\omega' G_0(i\omega-i\omega')W_0(i\omega')$$

Matrix form of χ_0

$$\chi^0(\boldsymbol{r},\boldsymbol{r}',i\omega)=2\sum_{m,n}\frac{(f_m-f_n)\psi_m^*(\boldsymbol{r})\psi_n(\boldsymbol{r})\psi_n^*(\boldsymbol{r}')\psi_m(\boldsymbol{r}')}{\epsilon_m-\epsilon_n-i\omega}$$

$$=\sum_{\mu,\nu}P_\mu(\boldsymbol{r})\chi^0_{\mu\nu}(i\omega)P_\nu(\boldsymbol{r}')$$

Auxiliary basis functions yet to be defined

Suppose

$$\psi_m^*(\boldsymbol{r})\psi_n(\boldsymbol{r})=\sum_\mu C^\mu_{mn}P_\mu(\boldsymbol{r}) \quad \rightarrow$$

$$\chi^0_{\mu\nu}(i\omega)=2\sum_{n,m}\frac{(f_m-f_n)C^\mu_{mn}C^\nu_{nm}}{\epsilon_m-\epsilon_n-i\omega}$$

Computational form of RPA

$$\chi^0(\boldsymbol{r},\boldsymbol{r}',i\omega)=\sum_{\mu,\nu} P_\mu(\boldsymbol{r})\chi^0_{\mu\nu}(i\omega)P_\nu(\boldsymbol{r}')$$

$$\mathrm{Tr}\left[\chi^0(i\omega)v\right]=\int d^3r\,d^3r'\,\chi^0(\boldsymbol{r},\boldsymbol{r}',i\omega)v(\boldsymbol{r}',\boldsymbol{r})=\sum_{\mu\nu}\chi^0_{\mu\nu}V_{\nu\mu}$$

$$V_{\nu\mu}=V_{\mu\nu}=\int d\boldsymbol{r}\,d\boldsymbol{r}'\,\frac{P_\mu(\boldsymbol{r})P_\nu(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}$$

Denoting:

$$\Pi_{\mu\nu}(i\omega)=\sum_\alpha \chi^0_{\mu\alpha}(i\omega)V_{\alpha\nu}\quad,\quad \tilde{\Pi}_{\mu\nu}(i\omega)=\sum_{\alpha,\beta} V^{1/2}_{\mu\alpha}\chi^0_{\alpha\beta}(i\omega)V^{1/2}_{\beta\nu}$$

$$E_c^{\mathrm{RPA}}=\frac{1}{2\pi}\int_0^\infty d\omega\,\mathrm{Tr}\left[\ln\left(1-\Pi(i\omega)\right)+\Pi(i\omega)\right]$$

$$=\frac{1}{2\pi}\int_0^\infty d\omega\,\mathrm{Tr}\left[\ln\left(1-\tilde{\Pi}(i\omega)\right)+\tilde{\Pi}(i\omega)\right]$$

$$=\frac{1}{2\pi}\int_0^\infty d\omega\left[\ln\left(\det\left(1-\tilde{\Pi}\right)\right)+\mathrm{Tr}\left(\tilde{\Pi}\right)\right]$$

Computational form of *GW*

$$W_{\mu,\nu}(i\omega)=\sum_{\alpha\beta} V^{1/2}_{\mu\alpha}\left[1-\tilde{\Pi}(i\omega)\right]^{-1}_{\alpha\beta} V^{1/2}_{\beta\nu}$$

G^0W^0 self-energy:

$$\Sigma^{GW}_n(i\omega)=-\frac{1}{2\pi}\sum_m \int_{-\infty}^{\infty} d\omega' \frac{1}{i\omega-i\omega'+\mu-\epsilon_m} \sum_{\mu\nu} O^{\mu}_{mn}\left[1-\tilde{\Pi}(i\omega)\right]^{-1} O^{\nu}_{mn}$$

$$O^{\mu}_{mn}=\sum_{\nu} C^{\nu}_{mn} V^{1/2}_{\nu\mu}$$

Analytical continuation: $\Sigma^{GW}_n(i\omega)\rightarrow\Sigma^{GW}_n(\omega)$

Ren, Rinke, Blum, Wieferink, Tkatchenko, Sanfilippo, Reuter, Scheffler, New. J. Phys. 14, 053020 (2012).

Key issues

- How to construct auxiliary basis set $\{P_\mu(\boldsymbol{r})\}$ to expand the products of Kohn-Sham orbitals $\{\psi_m^*(\boldsymbol{r})\psi_n(\boldsymbol{r})\}$, or rather the products of single-particle basis functions $\{\varphi_i(\boldsymbol{r})\varphi_j(\boldsymbol{r})\}$?
  - Plane waves: $e^{i(\boldsymbol{k}_1+\boldsymbol{G}_1)\cdot\boldsymbol{r}}e^{i(\boldsymbol{k}_2+\boldsymbol{G}_2)\cdot\boldsymbol{r}}=e^{i(\boldsymbol{k}_1+\boldsymbol{k}_2+\boldsymbol{G}_1+\boldsymbol{G}_2)\cdot\boldsymbol{r}}$
  - Gaussian: $e^{-\alpha_1|\boldsymbol{r}-\boldsymbol{R}_1|^2}e^{-\alpha_2|\boldsymbol{r}-\boldsymbol{R}_2|^2}=N\,e^{-(\alpha_1+\alpha_2)\left|\boldsymbol{r}-\frac{\alpha_1\boldsymbol{R}_1+\alpha_2\boldsymbol{R}_2}{\alpha_1+\alpha_2}\right|^2}$
  - Numerical orbitals: $\varphi_1(\boldsymbol{r}-\boldsymbol{R}_1)\varphi_2(\boldsymbol{r}-\boldsymbol{R}_2)=?$
- How to determine the expansion coefficient?

$$\psi_m^*(\boldsymbol{r})\psi_n(\boldsymbol{r})=\sum_\mu C_{mn}^\mu P_\mu(\boldsymbol{r})$$

$$=\sum_{i,j}c_{im}^*c_{jn}\varphi_i(\boldsymbol{r})\varphi_j(\boldsymbol{r})=\sum_{i.j.\mu}c_{\mathfrak{I}}^*c_{jn}O_{ij}^\mu P_\mu(\boldsymbol{r})$$

Construction of auxiliary basis sets

- For a given set of single-particle basis $\{\varphi_i(\boldsymbol{r}) = u_{nl}(\boldsymbol{r}) Y_{lm}(\hat{\boldsymbol{r}})\}$, construct a corresponding auxiliary basis set :

  $P_\mu(\boldsymbol{r}) = \xi_{kl}(r) Y_{lm}(\hat{\boldsymbol{r}})$, centering also at the nulcear positions.

- Determine the shape of the radial functions:

For each type of atom, and each $l <= l_{max}$

$\{u_{n_1,l_1}(r) u_{n_2,l_2}(r)\}$

for all n_1, n_2, and l_1, l_2 satisfying $|l_1 - l_2| <= l <= |l_1 + l_2|$

↓ Gram-Schmidt

$\xi_{kl}(\boldsymbol{r}), k = 1, \cdots k_{max}$

Inspired by Aryasetiawan and Gunnarsson, Phys Rev. B 49, 16214 (1994).

- Multiplying $\xi_{kl}(r)$ with $Y_{lm}(\hat{\boldsymbol{r}})$ for all atoms and angular momenta

Determine the expansion coefficents: resolution of identity (RI)

$$\phi_i(\mathbf{r})\phi_j(\mathbf{r}) \approx \sum_\mu C_{ij}^\mu P_\mu(\mathbf{r}); \qquad \left(\delta\rho(\mathbf{r}) = \phi_i(\mathbf{r})\phi_k(\mathbf{r}) - \sum_\mu C_{ik}^\mu P_\mu(\mathbf{r}).\right)$$

minimizing $(\delta\rho|\delta\rho)$

$$C_{ik}^\mu = \sum_\nu (ik\nu) S^{-1}_{\nu\mu}$$

$$\begin{aligned} (ik\nu) &= \int d\mathbf{r}\phi_i(\mathbf{r})\phi_k(\mathbf{r})P_\nu(\mathbf{r}) \\ S_{\nu\mu} &= \int d\mathbf{r}P_\nu(\mathbf{r})P_\mu(\mathbf{r}) \\ (ik|lj) &= \sum_{\mu\mu'\nu\nu'} (ik\nu)S^{-1}_{\nu\nu'}V_{\nu'\mu'}S^{-1}_{\mu'\mu}(\mu lj). \end{aligned}$$

"RI-SVS" version

minimizing $(\delta\rho|\delta\rho)$

$$C_{ik}^\mu = \sum_\nu (ik|\nu) V^{-1}_{\nu\mu}$$

$$\begin{aligned} (ik|\nu) &= \int d\mathbf{r}d\mathbf{r}'\phi_i(\mathbf{r})\phi_k(\mathbf{r})v(\mathbf{r}-\mathbf{r}')P_\nu(\mathbf{r}'). \\ V_{\nu\mu} &= \int d\mathbf{r}d\mathbf{r}'P_\nu(\mathbf{r})v(\mathbf{r}-\mathbf{r}')P_\mu(\mathbf{r}'). \\ (ik|lj) &= \sum_{\mu\nu}(ik|\nu)V^{-1}_{\nu\mu}(\mu|lj). \end{aligned}$$

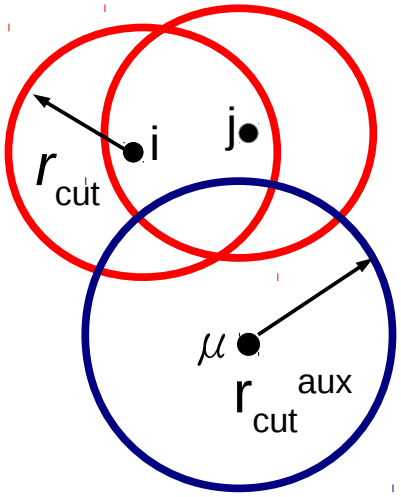
"RI-V" version

- "RI-V" gives much better accuracy
- A singular value decomposition ϵ^{svd} is introduced in the matrix inversion to prevent the possible illconditioning behavior.

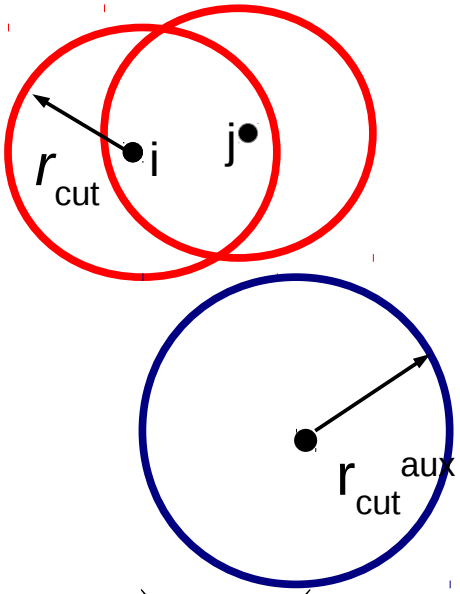
Dunlap, Connolly, and Sabin, JCP **71**, 3396 (1979).

Vahtras, J. Almlöf, and Feyereisen, CPL **213**, 514 (1993).

RI-SVS vs. RI-V



$$(\varphi_i \varphi_j P_\mu) \neq 0$$



$$(\varphi_i \varphi_j P_\mu) = 0 \quad (\varphi_i \varphi_j | P_\mu) \neq 0$$

- Our auxiliary basis construction procedure together with RI-V works for Hartree-Fock, MP2, RPA, GW, and other methodologies that require multi-center integrals.

Ren, Rinke, Blum, Wieferink, Tkatchenko, Sanfilippo, Reuter, Scheffler, New. J. Phys. 14, 053020 (2012).

Major steps in the RI-RPA implementation

0. Construct auxiliary basis set $\{P_\mu(\mathbf{r})\}$, size N_{aux} very cheap

I. Calculate the integrals $O(N^3)$, can be better for local basis

$$O^\mu_{mn} = \int \psi^*_m(\mathbf{r})\psi_n(\mathbf{r})v(\mathbf{r}-\mathbf{r}')P_\mu(\mathbf{r}'), \quad V_{\mu\nu} = \int P_\mu(\mathbf{r})v(\mathbf{r}-\mathbf{r}')P_\nu(\mathbf{r}')$$

II. Form $C^\nu_{mn} = \sum_\mu O^\mu_{mn} V^{-1/2}_{\mu\nu}$ $O(N^4)$

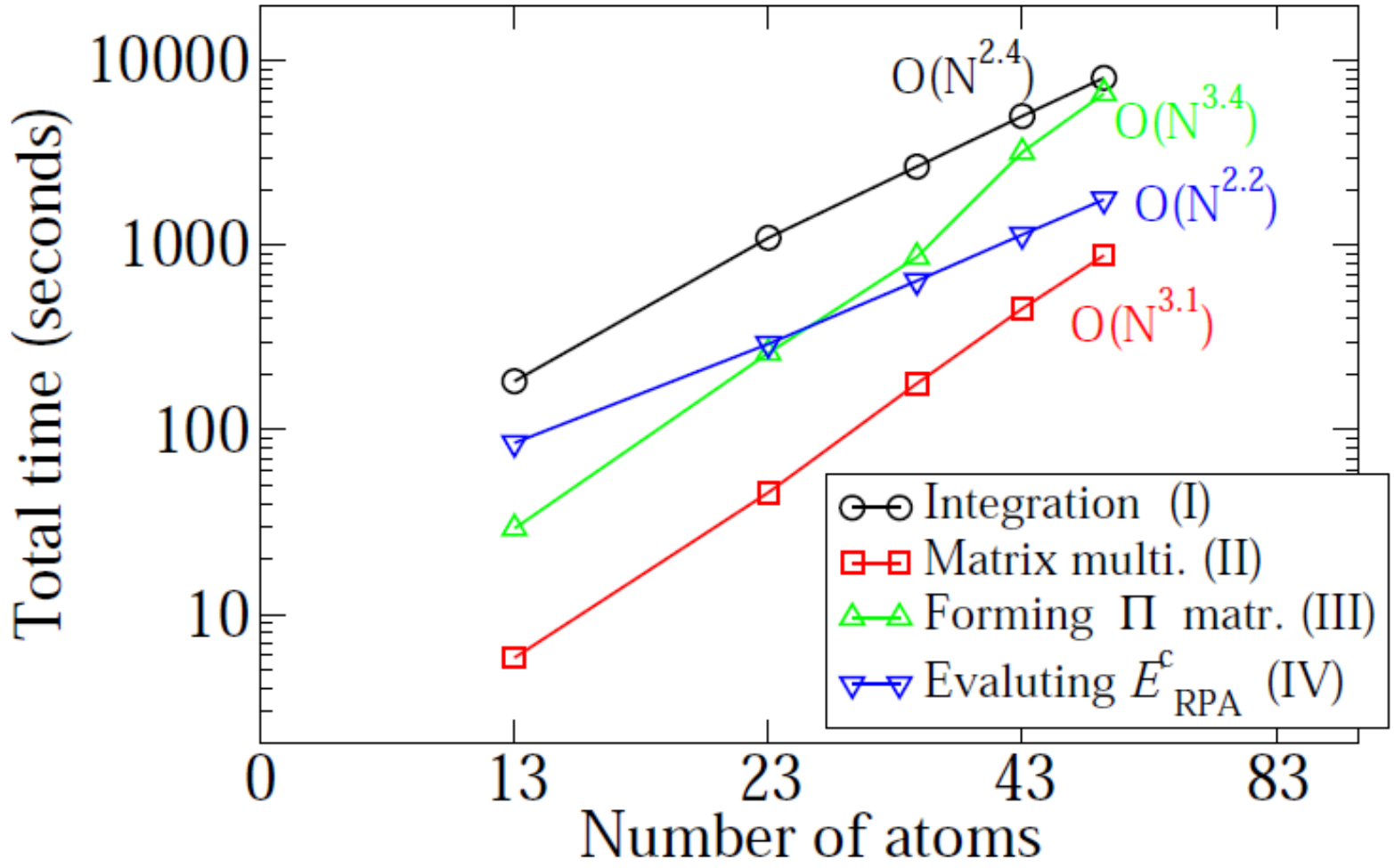
III. Build the matrix form of $\Pi_{\mu\nu}(i\omega)$ (size $N_{\text{aux}} \times N_{\text{aux}}$)

$$\Pi_{\mu\nu}(i\omega) = 2\sum_{mn} \frac{(f_m - f_n)C^\mu_{mn}C^\nu_{mn}}{i\omega - \epsilon_n + \epsilon_m} \quad O(N^4)$$

IV. Evaluate the RPA correlation energy (on a modified Gauss-Legendre frequency grid), and note $\mathrm{Tr}(\ln(A)) = \ln(\det(A))$

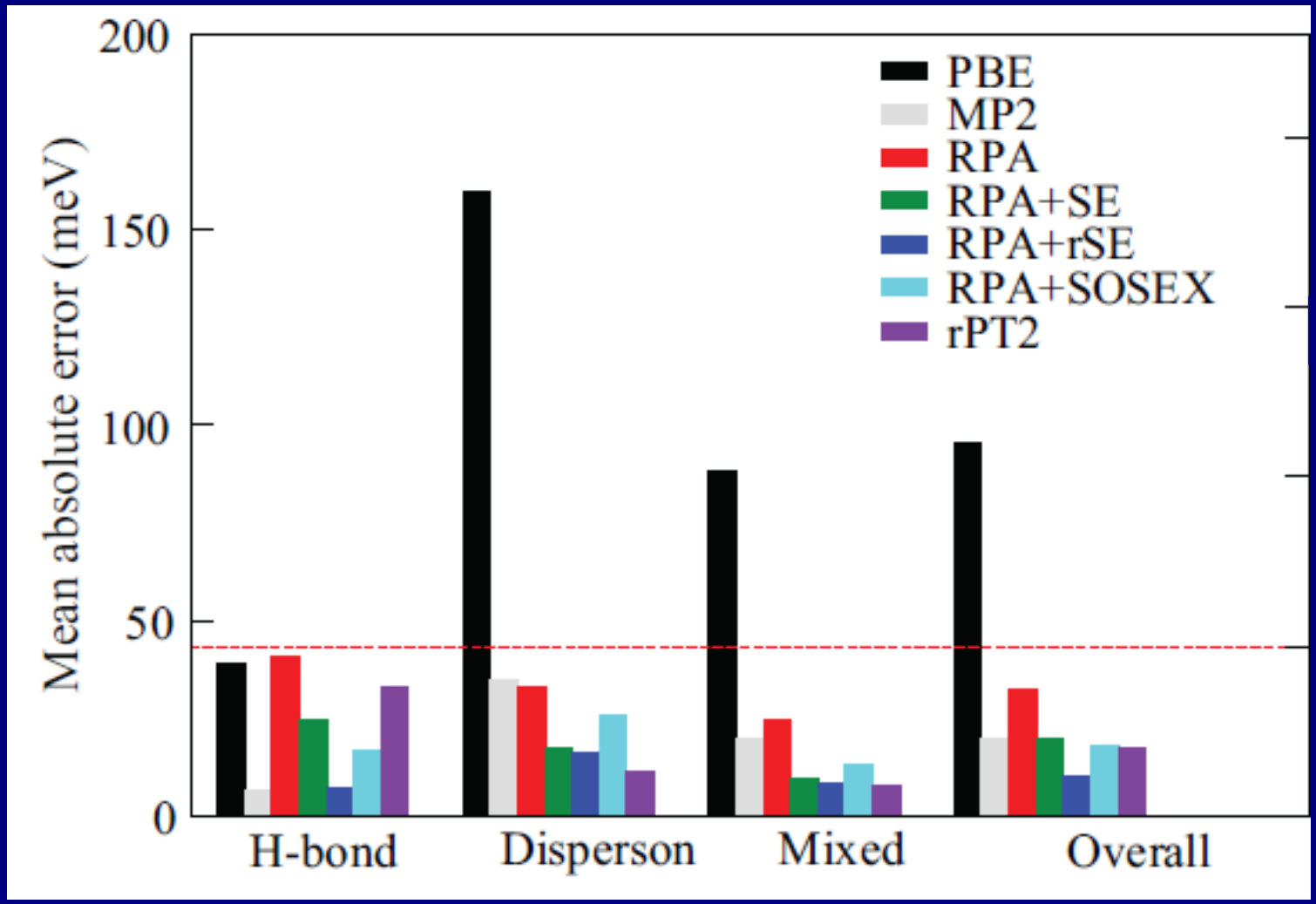
$$E_c^{\text{RPA}} = \frac{1}{2\pi}\int_0^\infty d\omega \left\{\ln\left[\det\left(1 - \Pi(i\omega)\right)\right] + \mathrm{Tr}[\Pi(i\omega)]\right\} \quad O(N^3)$$

Scaling behavior for RI-RPA (for a polyalanine chain)



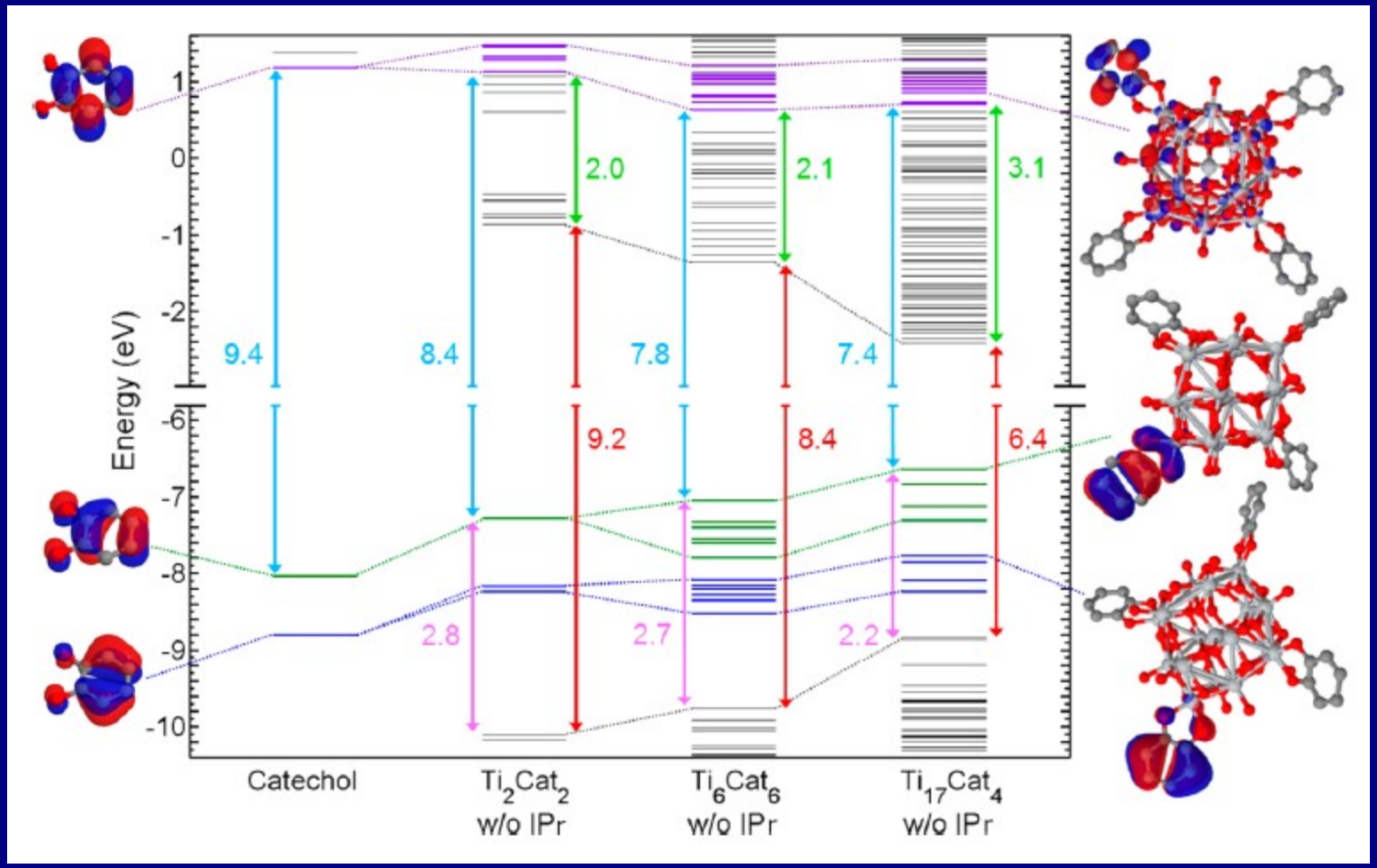
- NAO "tier 2" basis: N, C, O ($4s3p2d1f1g$); H ($4s2p1d$)
- Hardware: IBM Power 5, 16 CPU cores.

RPA and beyond for the S66 test set



Ren, Rinke, Scuseria, and Scheffler, Phys. Rev. B 88, 035120 (2013).

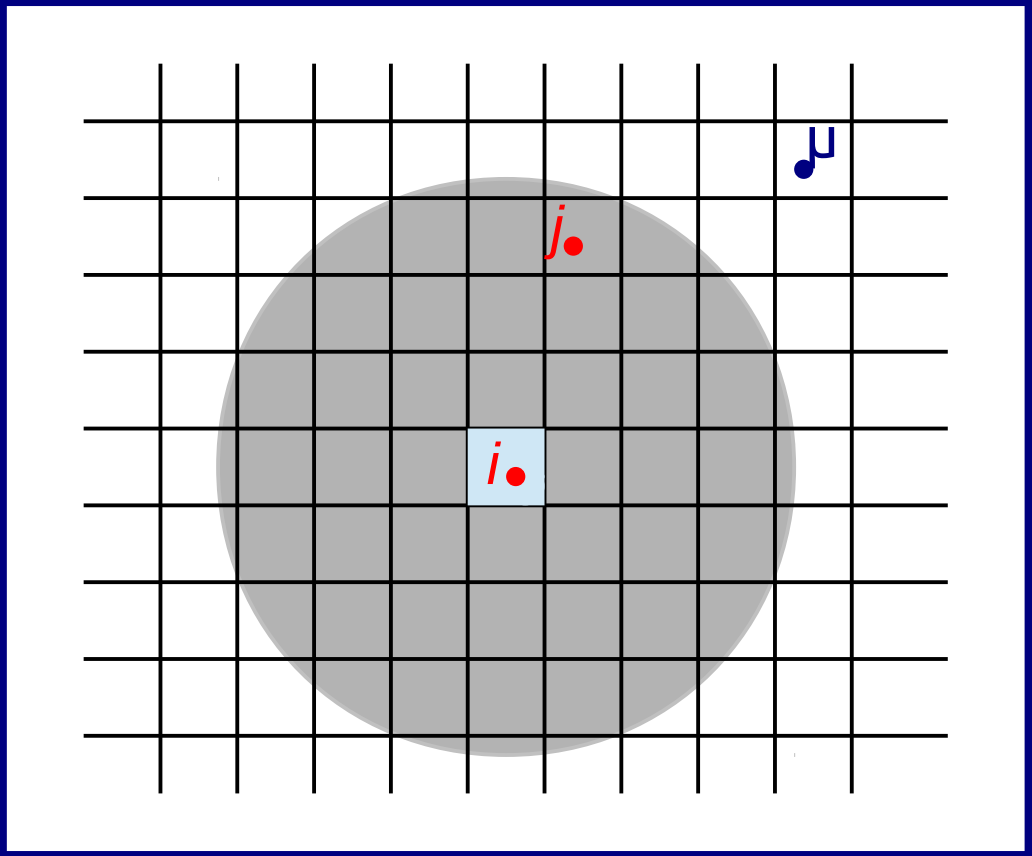
G^0W^0 applied to TiO2 clusters covered by catechol



Size effect of the interface level alignment between catechol and the increasingly large TiO2 clusters.

Marom, Körzdörfer, Ren, Tkatchenko, and Chelikowsky,
J. Phys. Chem. Lett. 14, 2395 (2014).

Localized RI (RI-LVL)

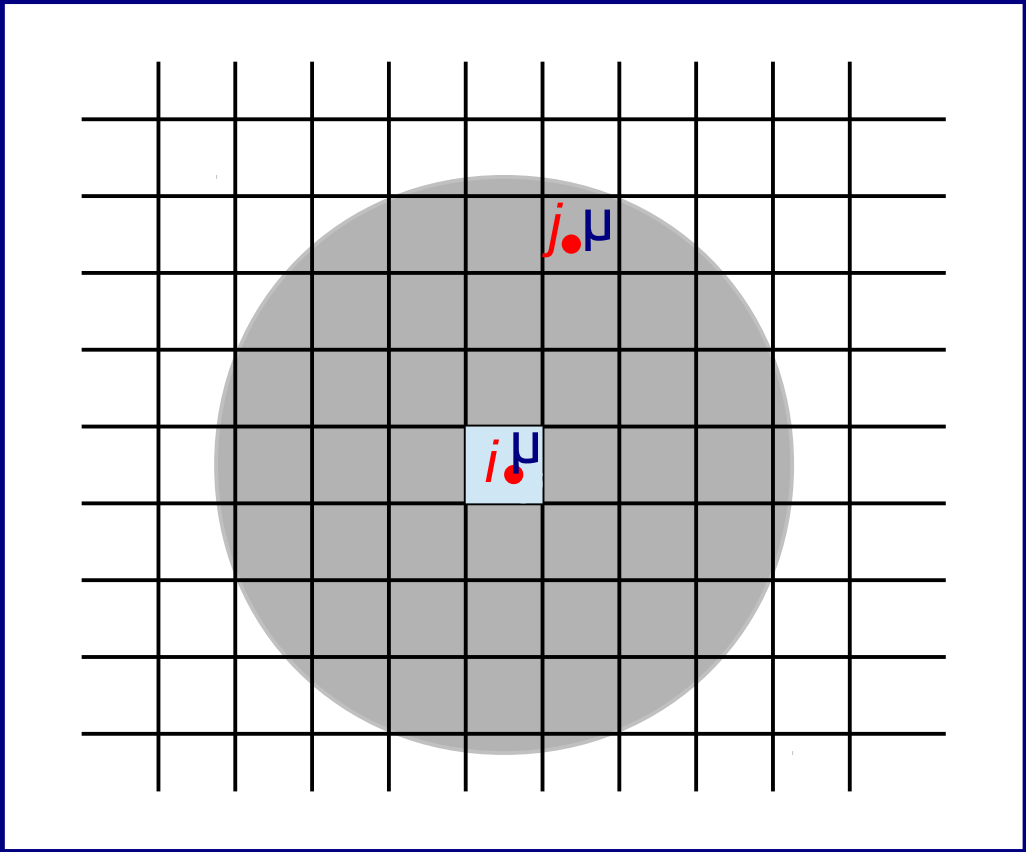


Number of atoms within the cutoff radius $O(10^2\text{-}10^3)$

Number of atoms on which $(ij|\mu)$ are significant: $O(10^5)$

RI-V is not the way to go!

Localized RI (RI-LVL)



Number of atoms within the cutoff radius $O(10^2\text{-}10^3)$

Number of atoms on which $(ij|\mu)$ are significant: $O(10^5)$

RI-V is not the way to go!

Localized RI, or RI-LVL (J. Wieferink)

$$\rho_{ij}(\boldsymbol{r}) = \varphi_i(\boldsymbol{r})\varphi_j(\boldsymbol{r}) \approx \sum_{\mu \in \{I,J\}} C_{ij}^{\mu} P_{\mu}(\boldsymbol{r})$$

I, J are atoms where i, j basis functions sit

Accuracy of RI-LVL

Minimizing $\left(\delta\rho_{ij}|\delta\rho_{ij}\right)$ $\Rightarrow$ $C_{ij}^{\mu} = \sum_{\nu\in\{I,\,J\}} (ij|\nu)\left[V^{IJ}\right]^{-1}_{\nu\mu}$

Block of the Coulom matrix with entries coming from atoms *I* and *J*

$$\Delta E = E\left(RI-LVL\right) - E\left(RI-V\right)$$

Root mean square deviation

S22 molecular set

RPA RI-LVL	ΔE_{tot} (meV)			
aux basis additions	per atom		systemwide	
	RMSD	MAX	RMSD	MAX
none	9.119	17.611	120.283	266.504
spdfgh(z=1)	0.040	0.120	0.214	0.467
g(z=1)	0.059	0.385	0.792	7.324
g(z=2)	0.060	0.383	0.795	7.286
g(z=3)	0.059	0.387	0.791	7.353
g(z=4)	0.058	0.390	0.785	7.416
g(z=5)	0.059	0.406	0.796	7.712
g(z=6)	0.058	0.417	0.804	7.932
g(z=7)	0.057	0.402	0.788	7.642

- Extra auxiliary basis functions are needed, but easy to add.

Wieferink, Ihrig, Zhang, Ropo, Ren, Rinke, Scheffler, and Blum, to be published

Periodic RPA

$$\chi^0_{\boldsymbol{k}}(\boldsymbol{r},\boldsymbol{r}';i\omega)=\frac{1}{N_{\boldsymbol{q}}}\sum_{\boldsymbol{q}}\frac{(f_{m,\boldsymbol{k}+\boldsymbol{q}}-f_{n,\boldsymbol{q}})\psi^*_{m,\boldsymbol{k}+\boldsymbol{q}}(\boldsymbol{r})\psi_{n,\boldsymbol{q}}(\boldsymbol{r})\psi^*_{n,\boldsymbol{q}}(\boldsymbol{r}')\psi_{m,\boldsymbol{k}+\boldsymbol{q}}(\boldsymbol{r}')}{\epsilon_{m,\boldsymbol{k}+\boldsymbol{q}}-\epsilon_{n,\boldsymbol{q}}-i\omega}$$

$$\psi^*_{m,\boldsymbol{k}+\boldsymbol{q}}(\boldsymbol{r})\psi_{n,\boldsymbol{q}}(\boldsymbol{r})=\sum_{\mu}C^{\mu,\boldsymbol{k}}_{m,\boldsymbol{k}+\boldsymbol{q};n,\boldsymbol{q}}P^*_{\mu,\boldsymbol{k}}(\boldsymbol{r})$$

$$\chi^0_{\boldsymbol{k}}(\boldsymbol{r},\boldsymbol{r}';i\omega)=\sum_{\mu,\nu}P^*_{\mu,\boldsymbol{k}}(\boldsymbol{r})\chi^0_{\mu\nu}(\boldsymbol{k},i\omega)P_{\nu,\boldsymbol{k}}(\boldsymbol{r}')$$

$$\chi^0_{\mu\nu}(\boldsymbol{k},i\omega)=\sum_{m,n,\boldsymbol{q}}\frac{(f_{m\boldsymbol{k}+\boldsymbol{q}}-f_{n,\boldsymbol{q}})C^{\mu,\boldsymbol{k}}_{m,\boldsymbol{k}+\boldsymbol{q};n,\boldsymbol{q}}C^{*\nu,\boldsymbol{k}}_{m,\boldsymbol{k}+\boldsymbol{q};n,\boldsymbol{q}}}{\epsilon_{m,\boldsymbol{k}+\boldsymbol{q}}-\epsilon_{n,\boldsymbol{q}}-i\omega}$$

Periodic RPA

$$\chi_{\boldsymbol{k}}^{0}(\boldsymbol{r},\boldsymbol{r}';i\omega)=\frac{1}{N_{\boldsymbol{q}}}\sum_{\boldsymbol{q}}\frac{(f_{m,\boldsymbol{k}+\boldsymbol{q}}-f_{n,\boldsymbol{q}})\psi_{m,\boldsymbol{k}+\boldsymbol{q}}^{*}(\boldsymbol{r})\psi_{n,\boldsymbol{q}}(\boldsymbol{r})\psi_{n,\boldsymbol{q}}^{*}(\boldsymbol{r}')\psi_{m,\boldsymbol{k}+\boldsymbol{q}}(\boldsymbol{r}')}{\epsilon_{m,\boldsymbol{k}+\boldsymbol{q}}-\epsilon_{n,\boldsymbol{q}}-i\omega}$$

$$\psi_{m,\boldsymbol{k}+\boldsymbol{q}}^{*}(\boldsymbol{r})\psi_{n,\boldsymbol{q}}(\boldsymbol{r})=\sum_{\mu}C_{m,\boldsymbol{k}+\boldsymbol{q};n,\boldsymbol{q}}^{\mu,\boldsymbol{k}}P_{\mu,\boldsymbol{k}}^{*}(\boldsymbol{r})$$

$$\chi_{\boldsymbol{k}}^{0}(\boldsymbol{r},\boldsymbol{r}';i\omega)=\sum_{\mu,\nu}P_{\mu,\boldsymbol{k}}^{*}(\boldsymbol{r})\chi_{\mu\nu}^{0}(\boldsymbol{k},i\omega)P_{\nu,\boldsymbol{k}}(\boldsymbol{r}')$$

$$\chi_{\mu\nu}^{0}(\boldsymbol{k},i\omega)=\sum_{m,n,\boldsymbol{q}}\frac{(f_{m\boldsymbol{k}+\boldsymbol{q}}-f_{n,\boldsymbol{q}})C_{m,\boldsymbol{k}+\boldsymbol{q};n,\boldsymbol{q}}^{\mu,\boldsymbol{k}}C_{m,\boldsymbol{k}+\boldsymbol{q};n,\boldsymbol{q}}^{*\nu,\boldsymbol{k}}}{\epsilon_{m,\boldsymbol{k}+\boldsymbol{q}}-\epsilon_{n,\boldsymbol{q}}-i\omega}$$

$$\psi_{m.\boldsymbol{k}+\boldsymbol{q}}^{*}(\boldsymbol{r})\psi_{n,\boldsymbol{q}}(\boldsymbol{r})=\sum_{i,j}c_{im}^{*}(\boldsymbol{k}+\boldsymbol{q})c_{jn}(\boldsymbol{q})\varphi_{i,\boldsymbol{k}+\boldsymbol{q}}^{*}(\boldsymbol{r})\varphi_{j,\boldsymbol{q}}(\boldsymbol{r})$$

$$\varphi_{j,\boldsymbol{q}}(\boldsymbol{r})=\sum_{\boldsymbol{R}}e^{i\boldsymbol{q}\cdot\boldsymbol{R}}\varphi_{j}(\boldsymbol{r}-\boldsymbol{R})$$

$$C_{m,\boldsymbol{k}+\boldsymbol{q};n,\boldsymbol{q}}^{\mu,\boldsymbol{k}}=\sum_{i,j}c_{im}^{*}(\boldsymbol{k}+\boldsymbol{q})c_{jn}(\boldsymbol{q})C_{i,\boldsymbol{k}+\boldsymbol{q};j,\boldsymbol{q}}^{\mu,\boldsymbol{k}}$$

$$\varphi_{i,\boldsymbol{k}+\boldsymbol{q}}^{*}(\boldsymbol{r})\varphi_{j,\boldsymbol{q}}(\boldsymbol{r})=\sum_{\mu}C_{i,\boldsymbol{k}+\boldsymbol{q};j,\boldsymbol{q}}^{\mu,\boldsymbol{k}}P_{\mu,\boldsymbol{k}}^{*}(\boldsymbol{r})$$

RI-LVL for periodic systems

$$\varphi^{*}_{i,\boldsymbol{k}+\boldsymbol{q}}(\boldsymbol{r})\varphi_{j,\boldsymbol{q}}(\boldsymbol{r})=\sum_{\mu} C^{\mu,\boldsymbol{k}}_{i,\boldsymbol{k}+\boldsymbol{q};j,\boldsymbol{q}} P^{*}_{\mu,\boldsymbol{k}}(\boldsymbol{r}) \qquad \text{(Eq. 1)}$$

$$\varphi^{*}_{i,\boldsymbol{k}+\boldsymbol{q}}(\boldsymbol{r})\varphi_{j,\boldsymbol{q}}(\boldsymbol{r})=\sum_{\boldsymbol{R},\boldsymbol{R}'} e^{-i(\boldsymbol{k}+\boldsymbol{q})\cdot\boldsymbol{R}} e^{i\boldsymbol{q}\cdot\boldsymbol{R}'} \varphi_i(\boldsymbol{r}-\boldsymbol{R})\varphi_j(\boldsymbol{r}-\boldsymbol{R}')$$

$$=\sum_{\boldsymbol{R},\boldsymbol{R}'} e^{-i(\boldsymbol{k}+\boldsymbol{q})\cdot\boldsymbol{R}} e^{i\boldsymbol{q}\cdot\boldsymbol{R}'} \sum_{\mu}\left[\tilde{C}^{\mu,\boldsymbol{R}}_{i\boldsymbol{R};j\boldsymbol{R}'} P_{\mu}(\boldsymbol{r}-\boldsymbol{R})+\tilde{C}^{\mu,\boldsymbol{R}'}_{i\boldsymbol{R};j\boldsymbol{R}'} P_{\mu}(\boldsymbol{r}-\boldsymbol{R}')\right]$$

(RI-LVL)

$$=\sum_{\boldsymbol{R},\boldsymbol{R}'} e^{-i(\boldsymbol{k}+\boldsymbol{q})\cdot\boldsymbol{R}} e^{i\boldsymbol{q}\cdot\boldsymbol{R}'} \sum_{\mu}\left[\tilde{C}^{\mu,\boldsymbol{0}}_{i\boldsymbol{0};j\boldsymbol{R}'-\boldsymbol{R}} P_{\mu}(\boldsymbol{r}-\boldsymbol{R})+\tilde{C}^{\mu,\boldsymbol{0}}_{i\boldsymbol{R}-\boldsymbol{R}';j\boldsymbol{0}} P_{\mu}(\boldsymbol{r}-\boldsymbol{R}')\right]$$

(Translational invariance)

$$=\sum_{\mu}\left[\tilde{C}^{\mu\boldsymbol{0}}_{i\boldsymbol{0};j,\boldsymbol{q}}+\tilde{C}^{\mu\boldsymbol{0}}_{i,-(\boldsymbol{k}+\boldsymbol{q});j,\boldsymbol{0}}\right] P^{*}_{\mu,\boldsymbol{k}}(\boldsymbol{r}) \qquad \text{(Eq. 2)}$$

Comparing Eq. 1 to Eq. 2,

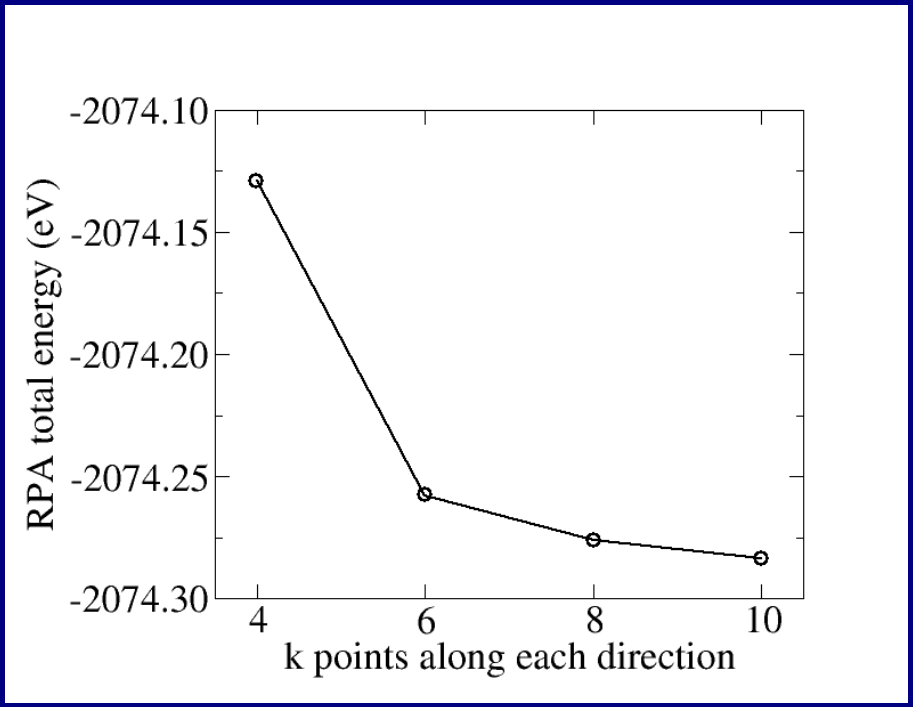
$$C^{\mu,\boldsymbol{k}}_{i,\boldsymbol{k}+\boldsymbol{q};j,\boldsymbol{q}}=\tilde{C}^{\mu\boldsymbol{0}}_{i\boldsymbol{0};j,\boldsymbol{q}}+\tilde{C}^{\mu\boldsymbol{0}}_{i,-(\boldsymbol{k}+\boldsymbol{q});j\boldsymbol{0}} \quad \text{or} \quad C^{\mu,\boldsymbol{k}-\boldsymbol{q}}_{i,\boldsymbol{k};j,\boldsymbol{q}}=\tilde{C}^{\mu\boldsymbol{0}}_{i\boldsymbol{0};j,\boldsymbol{q}}+\tilde{C}^{\mu\boldsymbol{0}}_{i,-\boldsymbol{k};j\boldsymbol{0}}$$

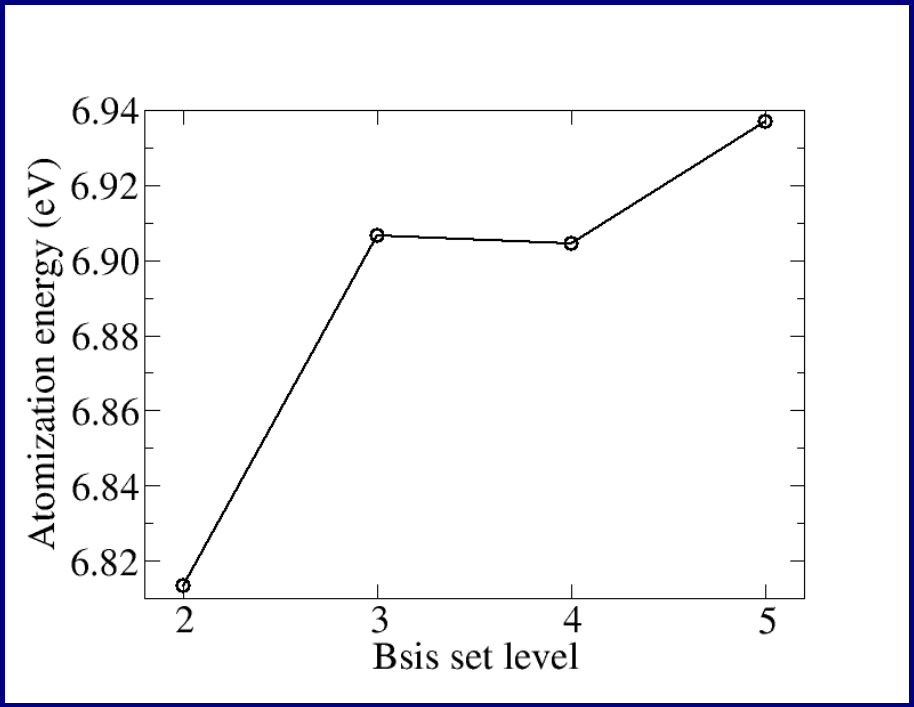
Convergence behavior of periodic RPA

Diamond, NAO-VCC-TZ

NAO-VCC-XZ(X=D,T,Q,5)

k mesh $6\times6\times6$





NAO-VCC-XZ basis set :

Zhang, Ren, Rinke, Blum, and Scheffler, New J. Phys. 15, 123033 (2013)

Some preliminary RPA results

RPA@PBE lattice constants and atomization energies for semiconductors and insulators

	Lattice constant (Å)			Atomization energy (eV)		
	this work	VASP[1]	Experiment	this work	VASP	Experiment
C	3.574	3.572	3.553	6.91	7.00	7.55
Si	5.492	5.432	5.421	4.25	4.39	4.55
NaCl	5.648	5.588	5.569	3.28	3.15	3.34
LiF	3.992	3.998	3.972	4.32	4.20	4.46

Computational setup in FHi-aims:
NAO-VCC-TZ basis set, $6\times6\times6$ ***k*** mesh,
Standard + one extra *g*(*z*=*6*) auxiliary basis set

[1] Harl, Schimka, Kresse, and Phys. Rev. B 81, 115126 (2010).

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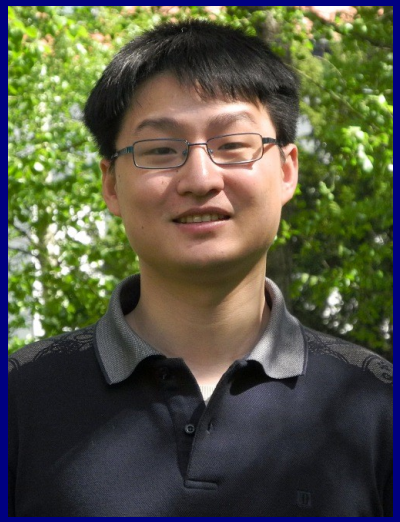

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Arvid Ihrig

and thank you ...