Basis-set-error free RPA correlation energy for atomic and diatomic system based on the Sternheimer equation

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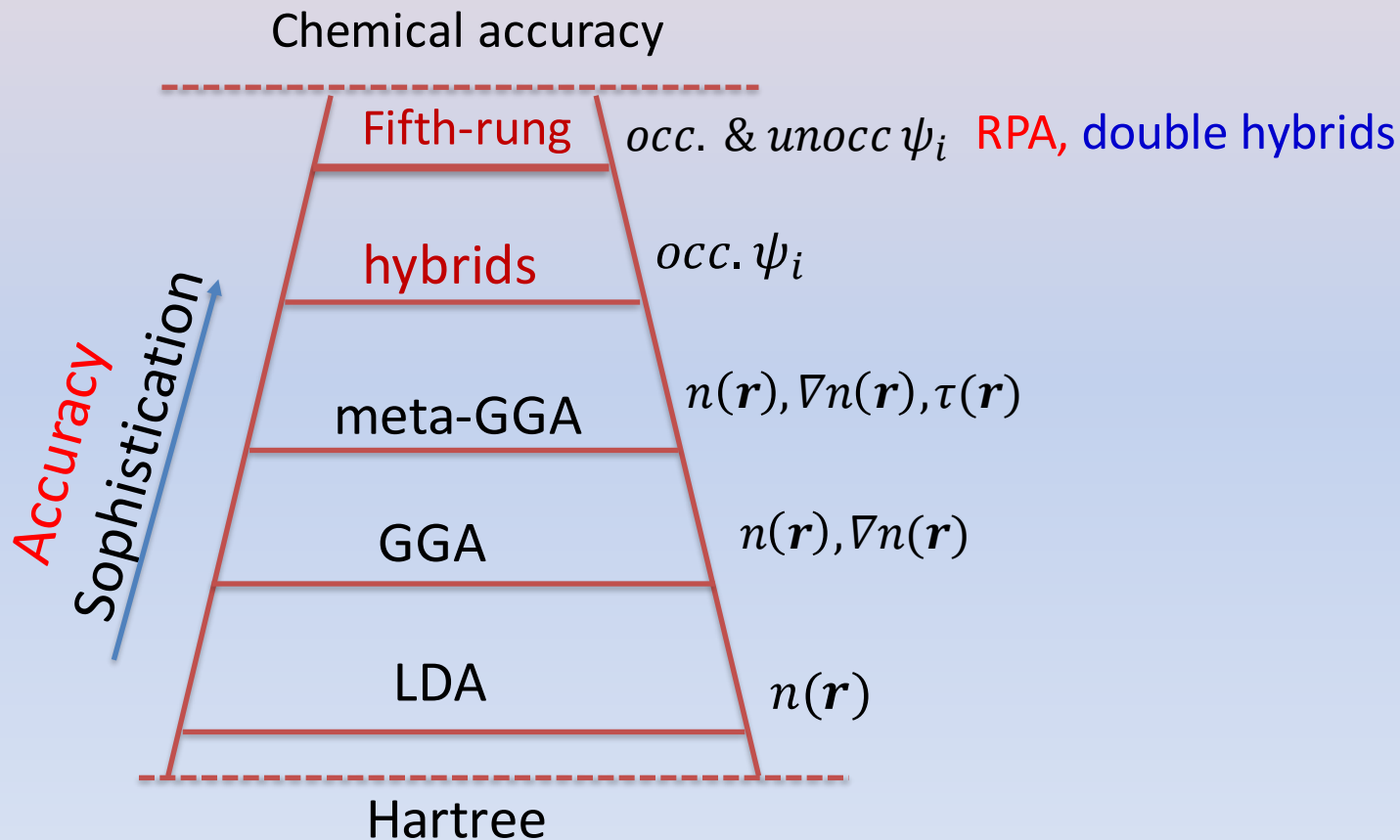Institute of Physics, Chinese Academy of Sciences, Beijing

Outline

- Introduction to random phase approximation (RPA) and the basis set issue

- Accurate RPA correlation energy for atoms based on the Sternheimer equation

- Solving the Sternheimer equation for diatomic molecules

- Outlook

Jacob's ladder in DFT

$$E_{\mathrm{KS}} = T_{\mathrm{s}} + V_{\mathrm{ext}} + E_{\mathrm{Hartree}} + E_{\mathrm{XC}}$$

Chemical accuracy

Fifth-rung — $occ. \& unocc \, \psi_i$ RPA, double hybrids

hybrids — $occ. \, \psi_i$

meta-GGA — $n(\boldsymbol{r}), \nabla n(\boldsymbol{r}), \tau(\boldsymbol{r})$

GGA — $n(\boldsymbol{r}), \nabla n(\boldsymbol{r})$

LDA — $n(\boldsymbol{r})$

Hartree

Accuracy
Sophistication

J. Perdew & K. Schmidt, in Density functional theory and its application to materials, edited by Van Doren e al. (2001).

RPA as a first-principles method

❖ With the framework of adiabatic-connection fluctuation-dissipation (ACFD) theorem, RPA can be formulated as an approximate, but fully nonlocal exchange-correlation (XC) energy functional.

The XC energy

The density response function

$$E_{\text{XC}} = -\frac{1}{2\pi} \int_0^1 d\lambda \int_0^\infty d\omega \int d\mathbf{r} d\mathbf{r}' \left[\chi_\lambda(\mathbf{r}, \mathbf{r}', i\omega) - n(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}') \right] v(\mathbf{r}, \mathbf{r}')$$

The coupling constant

Coulomb interaction

Langreth & Perdew, Phys. Rev. B **15**, 2884 (1977).
Gunnarsson & Lundqvist, Phys. Rev. B **13**, 4274 (1976).

Dyson equation for the linear response function:

$$\chi_\lambda = \chi_0 + \lambda \chi_0 \left(v + f_{xc}^\lambda \right) \chi_\lambda \, , \, f_{xc}^\lambda = 0 \, \rightarrow \, \chi_\lambda \approx \chi_\lambda^{\text{RPA}}$$

Explicitly known in terms of KS (both occupied and virtual) orbitals and orbital energies

$$\Longrightarrow \quad E_c^{\text{RPA}} = E_c^{\text{RPA}}[\epsilon_i, \psi_i]$$

Why is RPA interesting？

- Non-local electron correlation (including van der Waals interactions) seamlessly included.

- Many-electron screening effect well described -- hence suitable for metallic systems.

- Tests indicate that RPA can accurately describe delicate energy differences：
    - -- Adsorption energy differences
    - -- Energy difference between different polymorphs
    - -- Interaction strength and inter-layer distance of layered materials
    - -- Barrier heights of chemical reactions

Resolution of Identity Approach to RPA

$$\chi^0(\mathbf{r},\mathbf{r}',i\omega) = 2\sum_{i,j} \frac{(f_i - f_j)\psi_i^*(\mathbf{r})\psi_j(\mathbf{r})\psi_j^*(\mathbf{r}')\psi_i(\mathbf{r}')}{\varepsilon_i - \varepsilon_j - i\omega}$$

$$= \sum_{\mu,\nu} P_\mu(\mathbf{r})\chi_{\mu\nu}^0(i\omega)P_\nu(\mathbf{r}')$$

$$\psi_i^*(\mathbf{r})\psi_j(\mathbf{r}) = \sum_\mu C_{ij}^\mu P_\mu(\mathbf{r})$$

$$\chi_{\mu\nu}^0 (i\omega) = 2\sum_{i,j} \frac{(f_i - f_j)C_{ij}^\mu C_{ij}^\nu}{\varepsilon_i - \varepsilon_j - i\omega}$$

$$V_{\mu\nu} = \int d^3r\, d^3r' \frac{P_\mu(\mathbf{r})P_\nu(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

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

Basis set issue for RPA

$$\chi^0(\mathbf{r}, \mathbf{r}', i\omega) = 2 \sum_{i,j} \frac{(f_i - f_j)\psi_i^*(\mathbf{r})\psi_j(\mathbf{r})\psi_j^*(\mathbf{r}')\psi_i(\mathbf{r}')}{\varepsilon_i - \varepsilon_j - i\omega}$$

$$= 2 \sum_{i}^{occ} \sum_{j}^{unocc} \frac{\psi_i^*(\mathbf{r})\psi_j(\mathbf{r})\psi_j^*(\mathbf{r}')\psi_i(\mathbf{r}')}{\varepsilon_i - \varepsilon_j - i\omega} + c.c.$$

（For simplicity, only consider integer occupations）

- Convergence with respect to the number of occupied states (i.e., basis set size) is slow

- Practically one relies on converging energy differences (.e.g., binding energy) up to certain precision.

- "Correlation consistent" basis sets are preferred, which allow for extrapolation to the "complete basis set" limit.

NAO basis sets: current status in FHI-aims

- **FHI-aims-2009 ("*tier-n*") basis sets** (*Blum et al., CPC 180, 2175 (2009)*)
  generated based on the LDA energy for dimers and suitable for ground-state DFT/HF-type calculations.

- **NAO-VCC-nZ basis sets** (*Zhang et al., NJP 15, 123033 (2013)*)
  generated based on RPA@PBE energy for atoms and suitable for "correlated calculations". Officially available only for H-Ar.

- **"*tier-n* + aug", "*tier-n* + STO", or "*tier-n* + aug + STO"**
  suitable for *GW* or *GW*+BSE spectroscopy calculations.

  Ren et al., NJP 14, 053020 (2012); Ren et al. PRM 5, 013807 (2021); Yao et al., JCTC 18, 1569 (2022))

Remark: Basis set requirements for RPA and *GW* are different!

RPA: Energy difference between different atomic configurations, severe BSSE
GW: Energy difference between different electronic configurations

Challenges for developing NAO-VCC-*n*Z for heavy elements

- Optimizing the RPA total energy for atoms is very inefficient for binding energy calculations.

- Frozen-core approximation has to be used, but which core to freeze is tricky. Including semi-core states lead to too big basis sets

- The BFGS algorithm often got stuck in local minimum. One ends up with different basis sets with different "initial conditions".

- A lot of trial and errors

Alternative formulation of density response function

$$\chi^0(\mathbf{r},\mathbf{r}',i\omega) = 2 \sum_{i}^{occ} \sum_{j}^{unocc} \frac{\psi_i^*(\mathbf{r})\psi_j(\mathbf{r})\psi_j^*(\mathbf{r}')\psi_i(\mathbf{r}')}{\varepsilon_i - \varepsilon_j - i\omega} + c.c.$$

Where does this expression come from?

Physically, $\chi^0(\mathbf{r},\mathbf{r}',i\omega)$ describes the linear variation of the density upon a disturbance of the Kohn-Sham effective potential,
$$\chi^0(\boldsymbol{r},\boldsymbol{r}',i\omega) = \frac{\delta n(\boldsymbol{r},i\omega)}{\delta v_{eff}(\boldsymbol{r}',i\omega)}$$

$$n(\boldsymbol{r},i\omega) = 2 \sum_{i}^{occ} \psi_i^*(\boldsymbol{r})\psi_i(\boldsymbol{r}) \implies \delta n(\boldsymbol{r},i\omega) = 2 \sum_{i}^{occ} \psi_i^*(\boldsymbol{r})\delta\psi_i(\boldsymbol{r}) + c.c.$$

First-order perturbation theory:

$$\delta\psi_i(\boldsymbol{r}) = \sum_{j\neq i} \frac{\langle\psi_j|\delta v_{eff}|\psi_i\rangle}{\varepsilon_i - \varepsilon_j - i\omega}\psi_j(\boldsymbol{r}) \implies \frac{\delta\psi_i(\boldsymbol{r})}{\delta v_{eff}(\boldsymbol{r}',i\omega)} = \sum_{j\neq i} \frac{\psi_j^*(\boldsymbol{r}')\psi_i(\boldsymbol{r}')}{\varepsilon_i - \varepsilon_j - i\omega}\psi_j(\boldsymbol{r})$$

$$\frac{\delta n(\boldsymbol{r},i\omega)}{\delta v_{eff}(\boldsymbol{r}',i\omega)} = 2 \sum_{i}^{occ} \sum_{j\neq i} \frac{\psi_i^*(\mathbf{r})\psi_j(\mathbf{r})\psi_j^*(\mathbf{r}')\psi_i(\mathbf{r}')}{\varepsilon_i - \varepsilon_j - i\omega} + c.c.$$

(zero for $j \in occ$)

Alternative formulation of RI-RPA

$$\tilde{\chi}^0_{\mu\nu}(i\omega) = \iint d\boldsymbol{r}d\boldsymbol{r}' \, P_\mu(\boldsymbol{r})\chi^0(\boldsymbol{r},\boldsymbol{r}',i\omega)P_\nu(\boldsymbol{r}') = \int d\boldsymbol{r} \, P_\mu(\boldsymbol{r})n_\nu^{(1)}(\boldsymbol{r},i\omega)$$

$$n_\nu^{(1)}(\boldsymbol{r},i\omega) = \int d\boldsymbol{r}' \, \chi^0(\boldsymbol{r},\boldsymbol{r}',i\omega)P_\nu(\boldsymbol{r}') = \int d\boldsymbol{r}' \, \frac{\delta n(\boldsymbol{r},i\omega)}{\delta v_{eff}(\boldsymbol{r}',i\omega)} P_\nu(\boldsymbol{r}')$$

$\tilde{\chi}^0_{\mu\nu}(i\omega)$ can be understood as the projection of the linear density change upon a disturbance of $P_\nu(\boldsymbol{r})$ to a function $P_\mu(\boldsymbol{r})$.

$$\chi_{\mu\nu}(i\omega) = \sum_{\mu',\nu'} S_{\mu\mu'}^{-1} \tilde{\chi}^0_{\mu'\nu'}(i\omega) S_{\nu'\nu}^{-1} \qquad S_{\mu\nu} = \int d\boldsymbol{r} \, P_\mu(\boldsymbol{r})P_\nu(\boldsymbol{r})$$

How to determine first-order density $n_\nu^{(1)}(\boldsymbol{r},i\omega)$?

- Expanding $n_\nu^{(1)}(\boldsymbol{r},i\omega)$ in terms of the eigenspectrum of $\hat{H}_{KS}$ ➔ "Sum of States approach".
- Directly calculating $n_\nu^{(1)}(\boldsymbol{r},i\omega)$ by solving a differential equation.

The Sternheimer equation approach

$$n^{(1)}(\boldsymbol{r}, i\omega) = \delta n(\boldsymbol{r}, i\omega) = 2 \sum_{i}^{occ} \psi_i^*(\boldsymbol{r})\, \psi_i^{(1)}(\boldsymbol{r}, i\omega) + c.c.$$

$\psi_m^{(1)}(\boldsymbol{r}, i\omega)$ satisfies the so-called <u>Sternheimer equation</u>

$$\left[H^{(0)} - E_i^{(0)} + i\omega \right] \psi_i^{(1)}(\boldsymbol{r}, i\omega) = \left[E_i^{(1)} - V^{(1)} \right] \psi_i^{(0)}(\boldsymbol{r})$$

where

$$H^{(0)} \psi_i^{(0)}(\boldsymbol{r}) = E_i^{(0)} \psi_i^{(0)}(\boldsymbol{r})$$

$$E_i^{(1)} = \left\langle \psi_i^{(0)} \middle| V^{(1)} \middle| \psi_i^{(0)} \right\rangle \qquad V^{(1)}(\boldsymbol{r}) = P_v(\boldsymbol{r})$$

- Expanding $\psi_i^{(1)}(\boldsymbol{r}, i\omega)$ in terms of NAOs yields the same results as the SOS approach.

- Solving the Sternheimer equation on a real-space grid can go beyond the Hilbert space expanded by the finite NAO basis set.

Solving Sternheimer equation for a single atom

Simplifications for a single atom:

$$\psi_i^{(0)}(\boldsymbol{r}) = u_{il}^{(0)}(r) Y_{lm}(\theta, \varphi)$$

$$\psi_i^{(1)}(\boldsymbol{r}, i\omega) = \sum_{l'm'} u_{i,l'm'}^{(1)}(r, i\omega) Y_{l'm'}(\theta, \varphi)$$

$$V^{(1)}(\boldsymbol{r}) = P_v(\boldsymbol{r}) = V^{(1)}(r) Y_{LM}(\theta, \varphi)$$

$$\left(-\frac{1}{2r}\frac{\partial^2}{\partial r^2} r + \frac{l'(l'+1)}{2r^2} + V(r) - E_i^{(0)} + i\omega \right) u_{i,l'm'}^{(1)}(r, i\omega)$$

$$= G_{l'Ll}^{m'Mm} \left(E^{(1)} \delta_{l',l} \delta_{m',m} - V^{(1)}(r) \right) u_{il}^{(0)}(r)$$

The Sternheimer equation is reduced to an one-dimensional radial differential equation that can be solved by the finite difference method on a dense radial grid.

Implementation details

Using one-dimensional logarithmic grids from FHI-aims

N_{grid}:1000~2000 (decided by charge number Z)

$r(i) = r_{min} * r_{inc}^{(i-1)}, \quad r_{min} = 10^{-4}/Z, r_{max} \sim 100$ Bohr.

For simpler differentiation, we introduce coordinate transformation to convert logarithmic coordinate $r(i)$ to uniform coordinate $x(i)$, and the corresponding relationship is as follows, $x(i) = \ln(r(i)) = r_{min} + (i-1) * r_{inc}$

$$\frac{d}{dr} = e^{-x} \frac{d}{dx}$$

The derivatives can be expressed as:

$$f'(x(i)) = \frac{f(x(i+1)) - f(x(i-1))}{2\Delta x}$$

$$f''(x(i)) = \frac{f(x(i+1)) - 2f(x(i)) + f(x(i-1))}{\Delta x^2}$$

Implementation details

Define $f(r) = \sqrt{r}\, u^{(1)}(r)$

The one-dimensional Sternheimer equation in differential form can be written as

$$\left(-\frac{1}{2}\frac{f(x(i+1)) + f(x(i-1)) - 2f(x(i))}{\Delta x^2} + \frac{\left(l' + \frac{1}{2}\right)^2}{2} + r(x(i))^2 \left(V(r) - E_i^{(0)} + i\omega\right) \right) f(x(i))$$
$$= G_{l'Ll}^{m'Mm}\, r(x(i))^{5/2} \left(E^{(1)}\delta_{l',l}\delta_{m',m} - V^{(1)}(x(i))\right) u_{il}^{(0)}(x(i))$$

Finite difference transforms differential equations into linear equations $Af = B$

$$A = \begin{pmatrix} \frac{1}{\Delta x^2} + \frac{(l'+0.5)^2}{2} + r(1)^2(v_{eff}(1) - \epsilon_i + i\omega) & -\frac{1}{2\Delta x^2} & 0 & \cdots \\ -\frac{1}{2\Delta x^2} & \frac{1}{\Delta x^2} + \frac{(l'+0.5)^2}{2} + r(2)^2(v_{eff}(2) - \epsilon_i + i\omega) & -\frac{1}{2\Delta x^2} & \cdots \\ 0 & -\frac{1}{2\Delta x^2} & & \cdots & \cdots \\ \cdots & \cdots & & \cdots & \cdots \end{pmatrix}$$

$$B(i) = G_{l'Ll}^{m'Mm}\, r(x(i))^{5/2} \left(E^{(1)}\delta_{l',l}\delta_{m',m} - V^{(1)}(x(i))\right) u_{il}^{(0)}(x(i))$$

Basis set convergence for RPA correlation energy

Ne atom, RPA@LDA, NAO-VCC-nZ

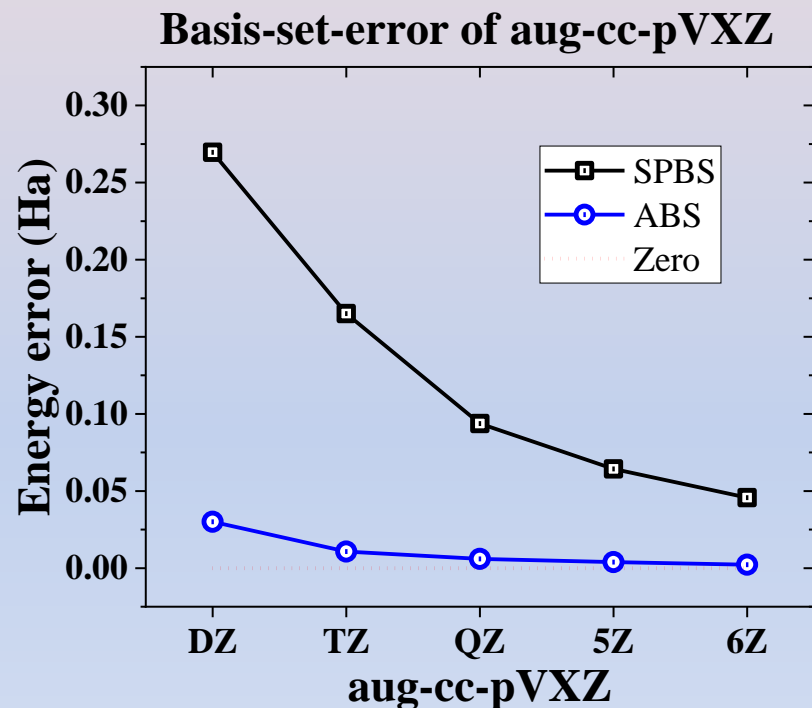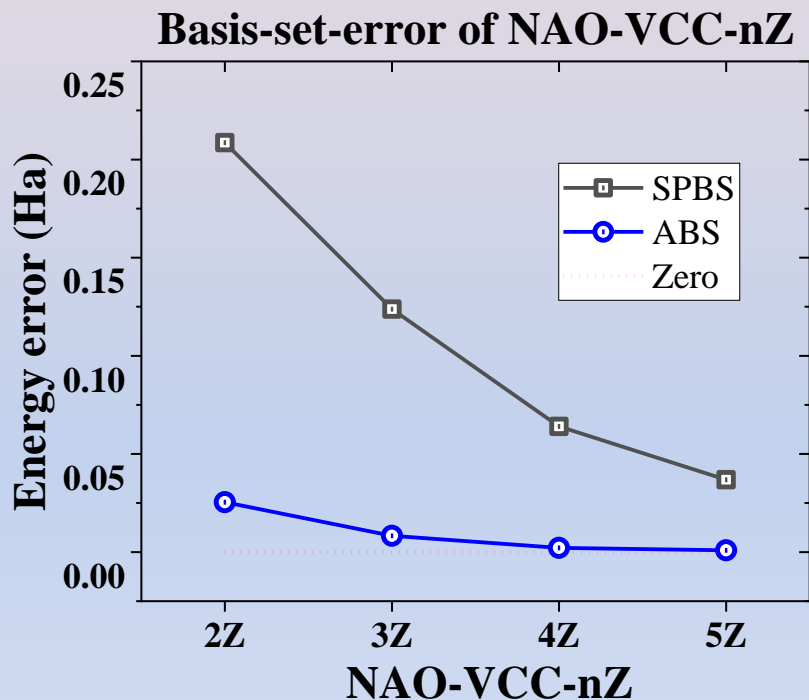**Ne atom, RPA@LDA, aug-cc-pVXZ**
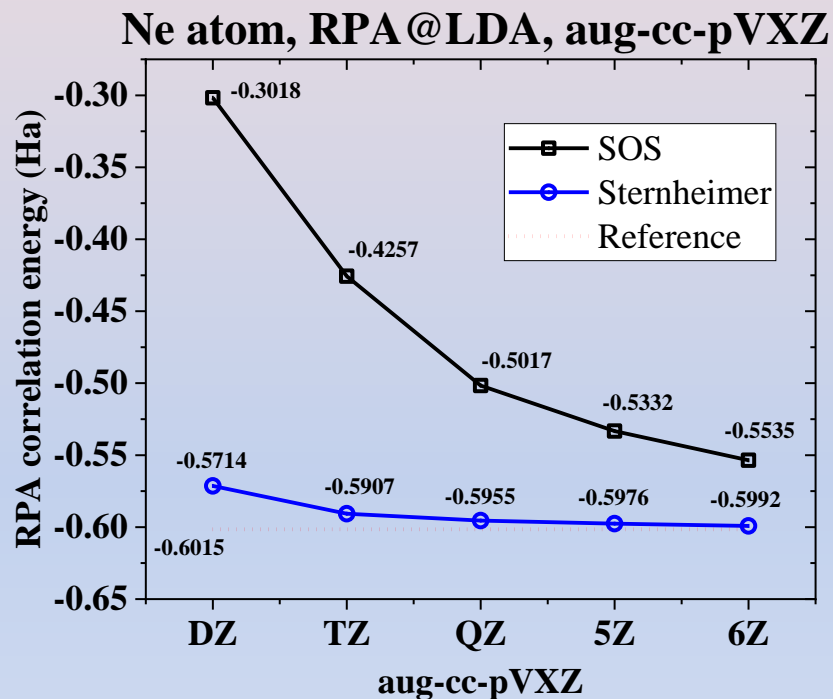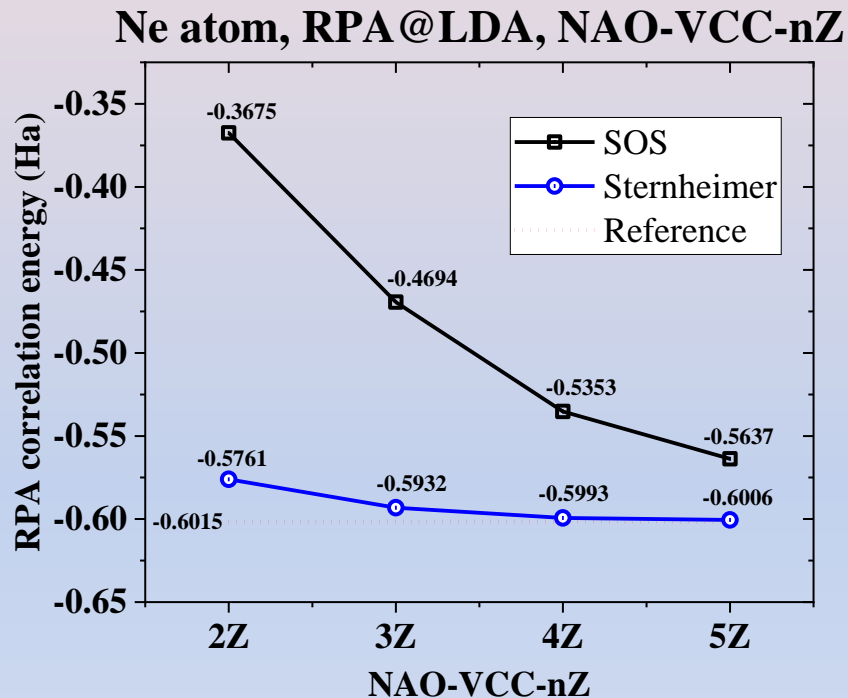
The Sternheimer results still depends on the auxiliary basis sets generated by the single particle orbitals.

Reference results are obtained using the "hard-wall cavity" method:

Jiang & Engel, JCP 127, 184108 (2007)
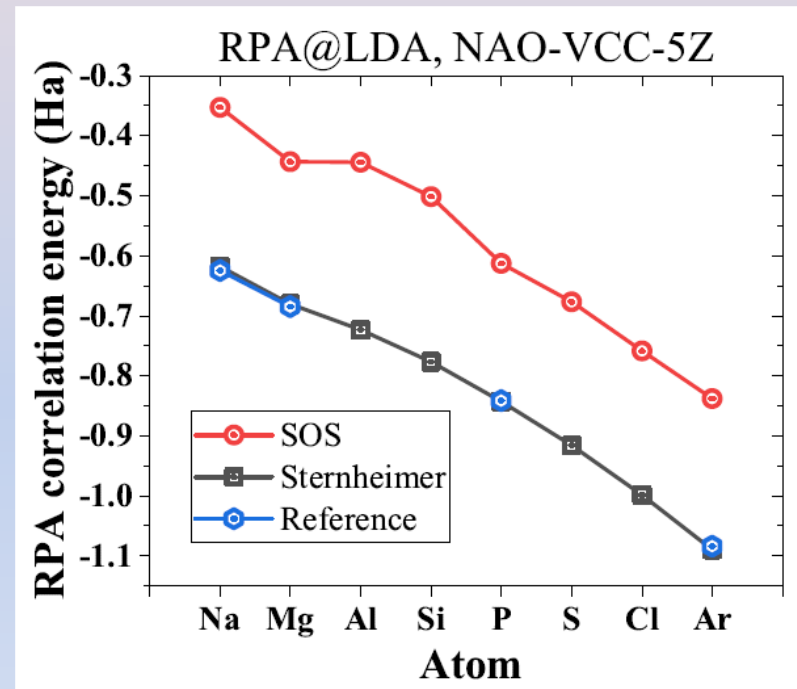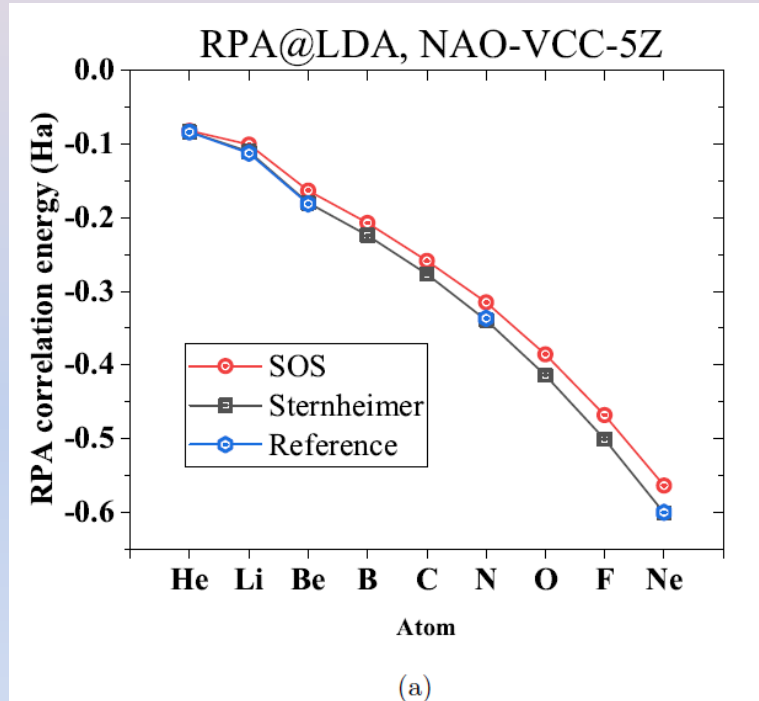
Distinguishing SPBS errors and ABS errors

SPBS: single-particle basis set; ABS: auxiliary basis set

Basis-set-error of NAO-VCC-nZ

Basis-set-error of aug-cc-pVXZ

$$\Delta^{(1)}\chi^0(\mathbf{r},\mathbf{r}',i\omega) = \chi^0(\mathbf{r},\mathbf{r}',i\omega) - \left(2\sum_i^{occ}\sum_j^{unocc} \frac{\psi_i^*(\mathbf{r})\psi_j(\mathbf{r})\psi_j^*(\mathbf{r}')\psi_i(\mathbf{r}')}{\varepsilon_i - \varepsilon_j - i\omega} + c.c. \right) : \text{SPBS error}$$

$$\Delta^{(2)}\chi^0(\mathbf{r},\mathbf{r}',i\omega) = \chi^0(\mathbf{r},\mathbf{r}',i\omega) - \left(\sum_{\mu,\nu} P_\mu(\mathbf{r})\, \chi_{\mu\nu}^0(i\omega) P_\nu(\mathbf{r}') \right) \quad : \text{ABS error}$$
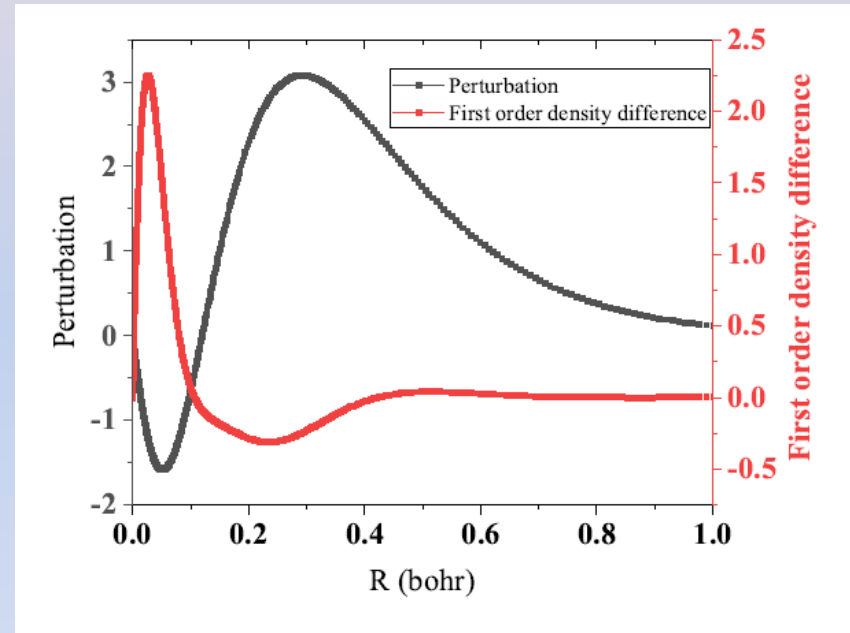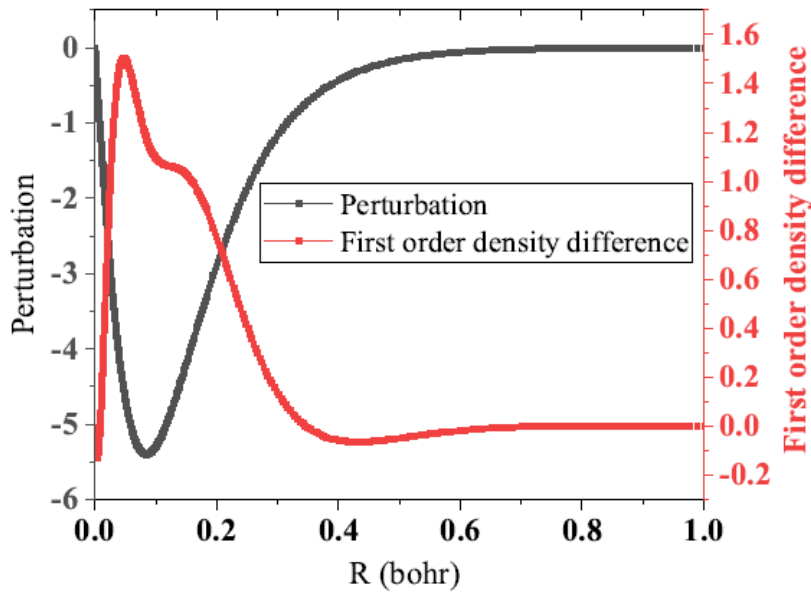
RPA correlation energy for other atoms

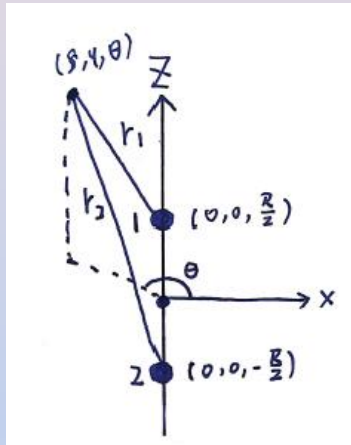Accurate RPA correlation energies for atoms from H to Kr are provided.

H. Peng, S. Yang, H. Jiang, H., Weng, X. Ren, arXiv:2306.11221

Visualizing the basis set error in real space

$$\delta n^{(1)}(r) = n^{(1)}_{\text{Sternheimer}} - n^{(1)}_{\text{SOS}}$$

Solving the Sternheimer equation for diatomic molecules

The ellipsoidal coordinate system
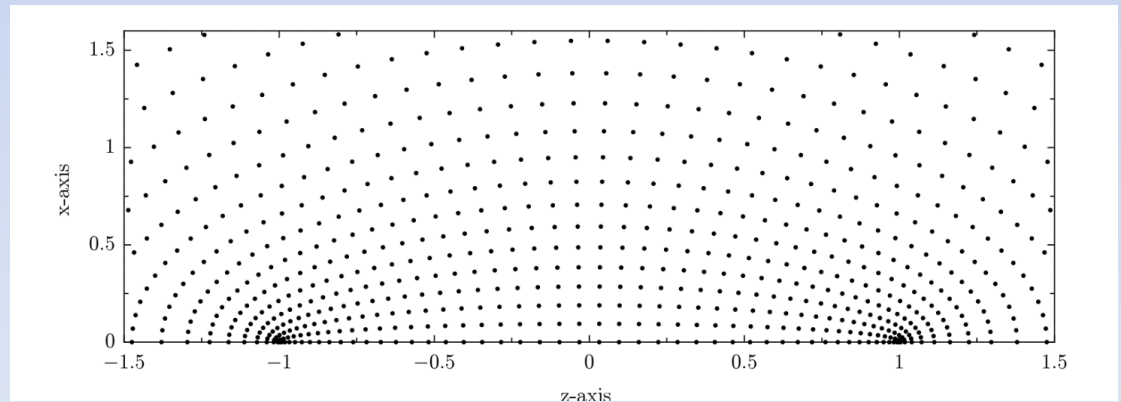
$$\xi = \frac{r_1 + r_2}{2}, \qquad 0 \le \xi < \infty$$

$$\eta = \frac{r_1 - r_2}{R}, \quad -1 \le \eta \le 1$$
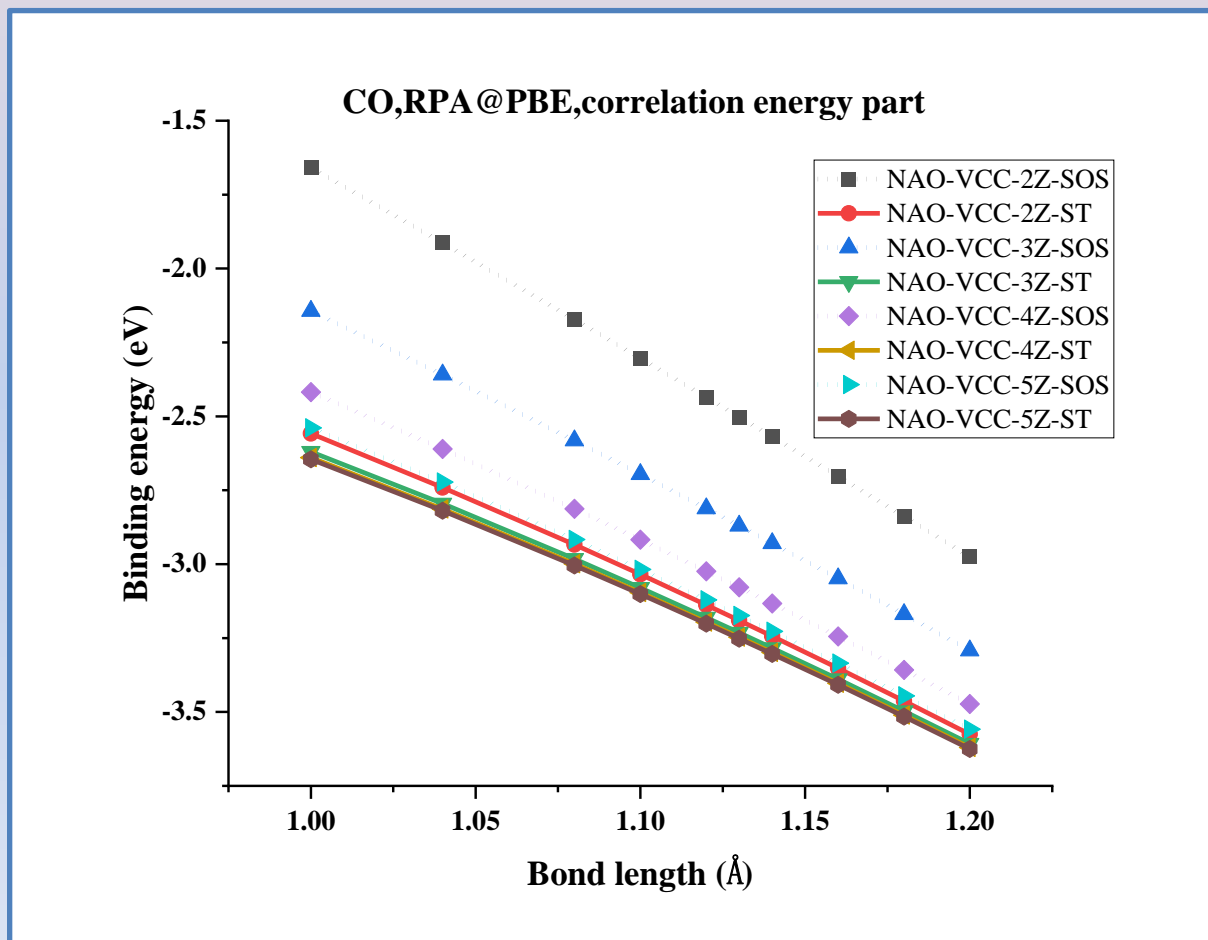
θ: azimuth angle, $0 \le \theta \le 2\pi$

For convenience, transforming the ellipsoidal coordinates (ξ, η, θ) are transformed into (μ, ν, θ) variables:

$$\mu = cosh^{-1}\xi \quad 0 \le \mu \le \infty$$
$$\nu = cos^{-1}\eta \qquad 0 \le \nu \le \pi$$

$$N_\mu = 120 \sim 180$$
$$N_\nu = 100 \sim 150$$
$$\mu(i) = (i-1) * h_\mu$$
$$\nu(i) = (i-1) * h_\nu$$

Convergence behavior for the CO molecule: The RPA correlation energy

CO,RPA@PBE,correlation energy part

Convergence behavior for the CO molecule: Total binding energy
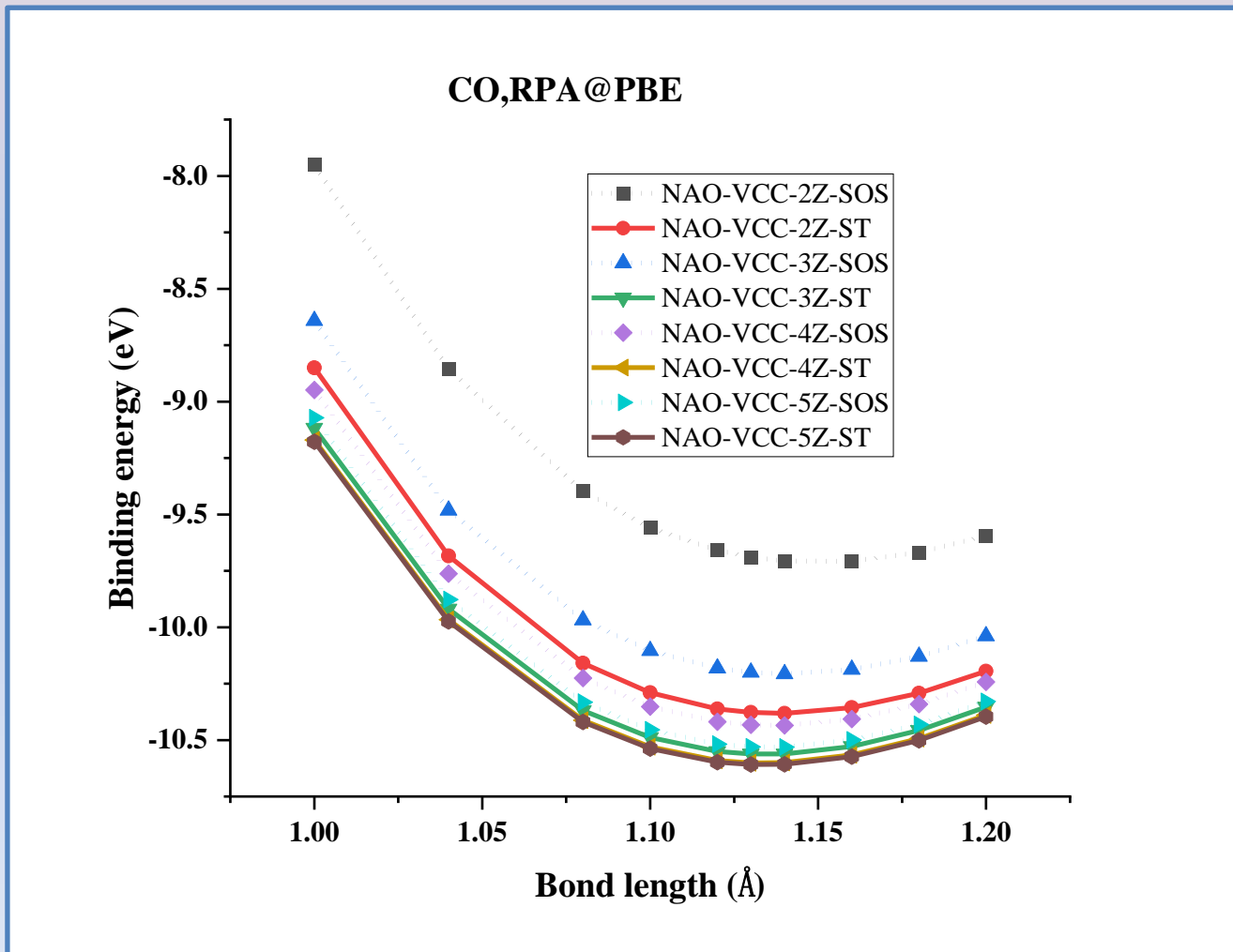
CO,RPA@PBE

RPA@PBE for N$_2$, all-electron versus frozen-core

N2,RPA@PBE,AE vs FC

Binding energy (KJ/mol)

- ■ NAO-VCC-5Z-SOS
- ● NAO-VCC-5Z-ST
- ▲ NAO-VCC-5Z-SOS-FC
- ▼ NAO-VCC-5Z-ST-FC

SOS:221.15
SOS_fc:220.13
ST:223.19
ST_fc:222.07

Bond length (Å)
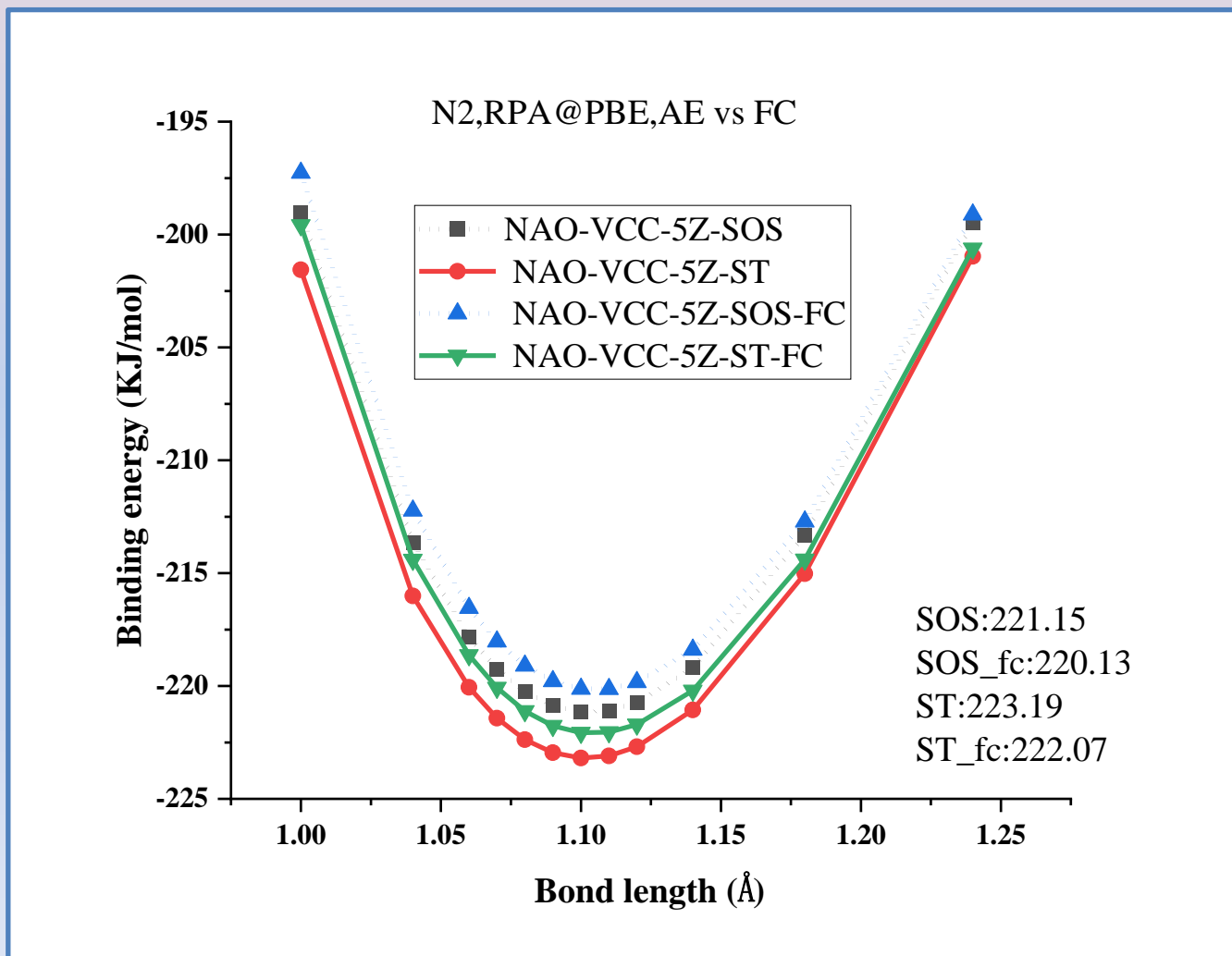
Summary and outlook

- Numerically precise RPA correlation energy are obtained for atoms and diatomic molecules by solving the Sternheimer equation on grids.

- The numerical technique allows to rigorously assess and monitor the finite atomic orbital basis set errors.

Outlook

- Extending the technique to *GW* (atoms and dimers)

- Generating optimized correlation consistent NAO basis sets guided by the reference data.

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