中国科学技术大学
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低标度实空间周期性 RPA 算法

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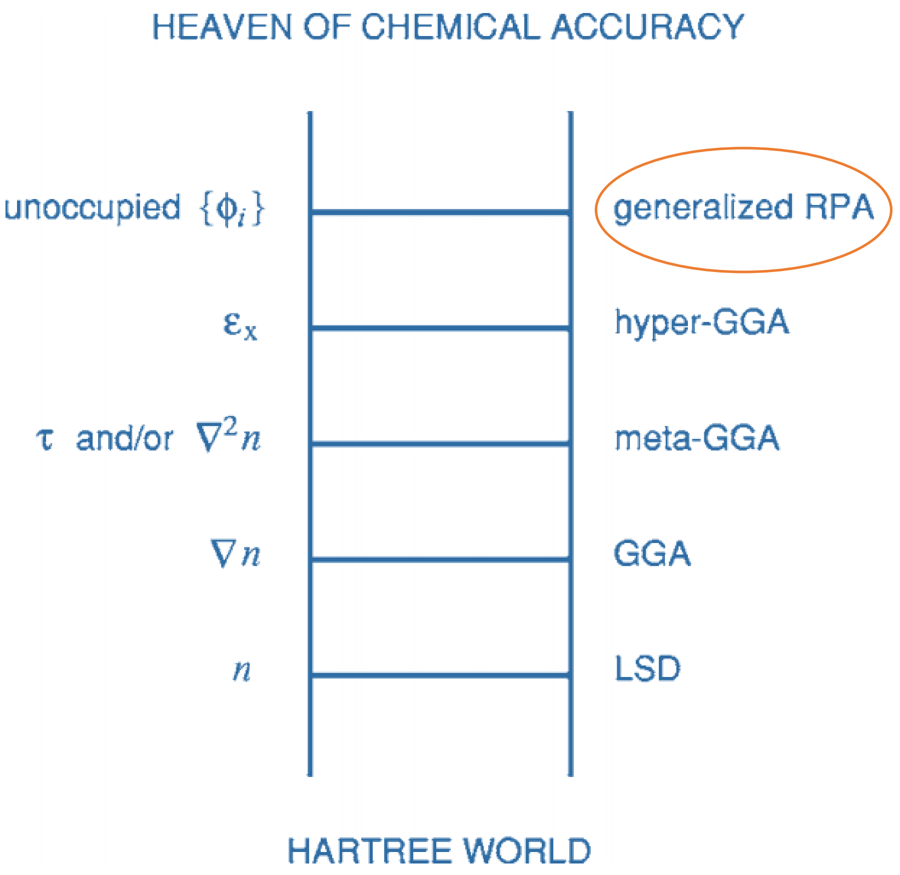
目录

DFT中的Jacob阶梯



RPA的优点:

- 自动包含范德瓦尔斯作用
- 处理不同的成键情况
- 兼容精确交换能，消除自相互作用误差

半局域近似的局限性:

- 具有混合成键特征的体系
- 强关联作用
- 激发态特征

无规相近似

从线性响应含时密度泛函理论出发:

真实体系密度响应函数: $\chi(\mathbf{r},\mathbf{r}',t-t') = \dfrac{\delta n(\mathbf{r},t)}{\delta v_{ext}(\mathbf{r}',t')}$

Kohn-Sham体系密度响应函数: $\chi^0(\mathbf{r},\mathbf{r}',t-t') = \dfrac{\delta n(\mathbf{r},t)}{\delta v_{eff}(\mathbf{r}',t')}$

$$v_{eff}[n](\mathbf{r},t) = v_{ext}(\mathbf{r},t) + v_H[n](\mathbf{r},t) + v_{xc}[n](\mathbf{r},t)$$

Dyson方程:

$$\chi(\mathbf{r},\mathbf{r}',\omega) = \chi^0(\mathbf{r},\mathbf{r}',\omega) + \int d^3r_1 d^3r_2 \chi^0(\mathbf{r},\mathbf{r}_1,\omega)\left(\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|} + f_{xc}(\mathbf{r}_1,\mathbf{r}_2.\omega)\right)\chi(\mathbf{r}_2,\mathbf{r}',\omega)$$

RPA: $f_{xc} = 0$

$$\chi^0(\mathbf{r},\mathbf{r}',i\omega) = \frac{1}{N_k^2}\sum_{n,m}\sum_{\mathbf{k},\mathbf{q}} \frac{(f_{n\mathbf{k}} - f_{m\mathbf{q}})\psi^*_{nk}(\mathbf{r})\psi_{m\mathbf{q}}(\mathbf{r})\psi^*_{m\mathbf{q}}(\mathbf{r}')\psi_{n\mathbf{k}}(\mathbf{r}')}{\epsilon_{nk} - \epsilon_{mq} - i\omega}$$

$O(N^4)$

实空间虚时域的无相互作用响应函数

无相互作用响应函数:

$$\chi^0(r,r',i\tau) = -iG^0(r,r',i\tau)G^0(r',r,-i\tau)$$

O(N^3)

$$G(\mathbf{r},\mathbf{r}',i\tau) = \Theta(\tau)\sum_a \varphi_a(\mathbf{r})\varphi_a^*(\mathbf{r}')\mathrm{e}^{-(\varepsilon_a-\varepsilon_F)\tau} - \Theta(-\tau)\sum_i \varphi_i(\mathbf{r})\varphi_i^*(\mathbf{r}')\mathrm{e}^{-(\varepsilon_i-\varepsilon_F)\tau}$$

虚时格林函数用局域原子轨道展开:

$$G^0(r,r',i\tau) = \sum_{ij}\sum_{\mathbf{R},\mathbf{R}'}\varphi_i(r-\mathbf{R})G_{ij}(\mathbf{R}'-\mathbf{R},i\tau)\varphi_j(r'-\mathbf{R}')$$

$$G_{ij}(\mathbf{R},i\tau) = \begin{cases} -\frac{1}{N_k}\sum_{n\mathbf{k}} f_{n\mathbf{k}}c_{i,n}(k)c^*_{j,n}(k)e^{-i\mathbf{k}\mathbf{R}}e^{-(\epsilon_{n,k}-\mu)\tau} & \tau <= 0 \\ \frac{1}{N_k}\sum_{n\mathbf{k}}(1-f_{n\mathbf{k}})c_{i,n}(k)c^*_{j,n}(k)e^{-i\mathbf{k}\mathbf{R}}e^{-(\epsilon_{n,k}-\mu)\tau} & \tau > 0 \end{cases}$$

从原子轨道表象到辅助基表象

$$\chi^0(r,r',i\tau) = -i\sum_{i,j,k,l}\sum_{\mathbf{R},\mathbf{R}',\mathbf{R}_1,\mathbf{R}_2}\varphi_i(r-\mathbf{R})\varphi_k(r-\mathbf{R}_1)G_{i,j}(\mathbf{R}'-\mathbf{R},i\tau)G_{l,k}(\mathbf{R}_1-\mathbf{R}_2,-i\tau)$$
$$\varphi_j(r'-\mathbf{R}')\varphi_l(r'-\mathbf{R}'_2)$$

使用局域单位元分解技术(LRI)，将轨道的乘积用一组辅助积展开：

$$\begin{aligned}\varphi_i(r-\mathbf{R})\varphi_k(r-\mathbf{R}_1) &\approx \sum_{\mu\in I} C^{\mu(\mathbf{R})}_{i(\mathbf{R}),k(\mathbf{R}_1)}P_\mu(r-\mathbf{R}) + \sum_{\mu\in K} C^{\mu(\mathbf{R}_1)}_{i(\mathbf{R}),k(\mathbf{R}_1)}P_\mu(r-\mathbf{R}_1)\\ &= \sum_{\mu\in I} C^{\mu(\mathbf{0})}_{i(\mathbf{0}),k(\mathbf{R}_1-\mathbf{R})}P_\mu(r-\mathbf{R}) + \sum_{\mu\in K} C^{\mu(\mathbf{0})}_{i(\mathbf{R}-\mathbf{R}_1),k(\mathbf{0})}P_\mu(r-\mathbf{R}_1)\end{aligned}$$

$$\chi^0(r,r',i\tau) = \sum_{\mu,\nu,\mathbf{R},\mathbf{R}'} P_\mu(r-\mathbf{R})\chi^0_{\mu,\nu}(\mathbf{R}'-\mathbf{R},i\tau)P_\nu(r'-\mathbf{R}')$$

实空间响应函数的矩阵形式

$$\chi^0(r, r', i\tau) = \sum_{\mu,\nu,\mathbf{R},\mathbf{R}'} P_\mu(r - \mathbf{R})\chi^0_{\mu,\nu}(\mathbf{R}' - \mathbf{R}, i\tau)P_\nu(r' - \mathbf{R}')$$

$$\begin{aligned}
\chi^0_{\mu,\nu}(\mathbf{R}, i\tau) &= \chi^{0(A)}_{\mu,\nu}(\mathbf{R}, i\tau) + \chi^{0(B)}_{\mu,\nu}(\mathbf{R}, i\tau) + \chi^{0(C)}_{\mu,\nu}(\mathbf{R}, i\tau) + \chi^{0(D)}_{\mu,\nu}(\mathbf{R}, i\tau) \\
&= -i\Bigg[\sum_{i\in\mathcal{U},j\in\mathcal{V}}\sum_{k,\mathbf{R}_1}\sum_{l,\mathbf{R}_2} C^{\mu(\mathbf{0})}_{i(\mathbf{0}),k(\mathbf{R}_1)} G_{l,k}(\mathbf{R}_1 - \mathbf{R}_2, -i\tau) C^{\nu(\mathbf{0})}_{j(\mathbf{0}),l(\mathbf{R}_2-\mathbf{R})} G_{i,j}(\mathbf{R}, i\tau) \\
&\quad + \sum_{i\in\mathcal{U},l\in\mathcal{V}}\sum_{k,\mathbf{R}_1}\sum_{j,\mathbf{R}_2} C^{\mu(\mathbf{0})}_{i(\mathbf{0}),k(\mathbf{R}_1)} G_{l,k}(\mathbf{R}_1 - \mathbf{R}, -i\tau) C^{\nu(\mathbf{0})}_{j(\mathbf{R}_2-\mathbf{R}),l(\mathbf{0})} G_{i,j}(\mathbf{R}_2, i\tau) \\
&\quad + \sum_{k\in\mathcal{U},j\in\mathcal{V}}\sum_{i,\mathbf{R}_1}\sum_{l,\mathbf{R}_2} C^{\mu(\mathbf{0})}_{i(\mathbf{R}_1),k(\mathbf{0})} G_{i,j}(\mathbf{R} - \mathbf{R}_1, i\tau) C^{\nu(\mathbf{0})}_{j(\mathbf{0}),l(\mathbf{R}_2-\mathbf{R})} G_{l,k}(-\mathbf{R}_2, -i\tau) \\
&\quad + \sum_{k\in\mathcal{U},l\in\mathcal{V}}\sum_{i,\mathbf{R}_1}\sum_{j,\mathbf{R}_2} C^{\mu(\mathbf{0})}_{i(\mathbf{R}_1),k(\mathbf{0})} G_{i,j}(\mathbf{R}_2 - \mathbf{R}_1, i\tau) C^{\nu(\mathbf{0})}_{j(\mathbf{R}_2-\mathbf{R}),l(\mathbf{0})} G_{l,k}(-\mathbf{R}, -i\tau)\Bigg]
\end{aligned}$$

公式化简

考虑指标互换与实空间格林函数的对称性，将响应函数公式化简：

$$
\begin{aligned}
\chi^0_{\mu,\nu}(\mathbf{R}, i\tau) = -i \Bigg[\sum_{i\in\mathcal{U}} \sum_{k,\mathbf{R}_1} C^{\mu(0)}_{i(0),k(\mathbf{R}_1)} \Bigg(& \sum_{j\in\mathcal{V}} G_{i,j}(\mathbf{R}, i\tau) \sum_{l,\mathbf{R}_2} C^{\nu(0)}_{j(0),l(\mathbf{R}_2-\mathbf{R})} G_{l,k}(\mathbf{R}_1 - \mathbf{R}_2, -i\tau) \\
& + \sum_{j\in\mathcal{V}} G^*_{i,j}(\mathbf{R}, -i\tau) \sum_{l,\mathbf{R}_2} C^{\nu(0)}_{j(0),l(\mathbf{R}_2-\mathbf{R})} G^*_{l,k}(\mathbf{R}_1 - \mathbf{R}_2, i\tau) \\
& + \sum_{j\in\mathcal{V}} G_{j,k}(\mathbf{R}_1 - \mathbf{R}, -i\tau) \sum_{l,\mathbf{R}_2} C^{\nu(0)}_{j(0),l(\mathbf{R}_2-\mathbf{R})} G_{i,l}(\mathbf{R}_2, i\tau) \\
& + \sum_{j\in\mathcal{V}} G^*_{j,k}(\mathbf{R}_1 - \mathbf{R}, i\tau) \sum_{l,\mathbf{R}_2} C^{\nu(0)}_{j(0),l(\mathbf{R}_2-\mathbf{R})} G^*_{i,l}(\mathbf{R}_2, -i\tau) \Bigg) \Bigg] \\
= -i \Bigg[\sum_{i\in\mathcal{U}} \sum_{k,\mathbf{R}_1} C^{\mu(0)}_{i(0),k(\mathbf{R}_1)} \Big(& M^{\nu}_{i,k}(\mathbf{R}_1, \mathbf{R}, i\tau) + M^{\nu*}_{i,k}(\mathbf{R}_1, \mathbf{R}, -i\tau) \\
& + Z^{\nu}_{i,k}(\mathbf{R}_1, \mathbf{R}, i\tau) + Z^{\nu*}_{i,k}(\mathbf{R}_1, \mathbf{R}, -i\tau) \Big) \Bigg]
\end{aligned}
$$

其中：

$$
M^{\nu}_{i,k}(\mathbf{R}_1, \mathbf{R}, i\tau) = \sum_{j\in\mathcal{V}} G_{i,j}(\mathbf{R}, i\tau) N^{\nu}_{j,k}(\mathbf{R}_1, \mathbf{R}, i\tau)
$$

$$
N^{\nu}_{j,k}(\mathbf{R}_1, \mathbf{R}, i\tau) = \sum_{l,\mathbf{R}_2} C^{\nu(0)}_{j(0),l(\mathbf{R}_2-\mathbf{R})} G_{l,k}(\mathbf{R}_1 - \mathbf{R}_2, -i\tau)
$$

$$
Z^{\nu}_{i,k}(\mathbf{R}_1, \mathbf{R}, i\tau) = \sum_{j\in\mathcal{V}} G_{j,k}(\mathbf{R}_1 - \mathbf{R}, -i\tau) X^{\nu}_{i,j}(\mathbf{R}_1, \mathbf{R}, i\tau)
$$

$$
X^{\nu}_{i,j}(\mathbf{R}_1, \mathbf{R}, i\tau) = \sum_{l,\mathbf{R}_2} C^{\nu(0)}_{j(0),l(\mathbf{R}_2-\mathbf{R})} G_{i,l}(\mathbf{R}_2, i\tau)
$$

实空间虚时响应函数

无相互作用响应函数

$$\chi^0(\mathbf{r},\mathbf{r}',i\tau) = -iG^0(\mathbf{r},\mathbf{r}',i\tau)G^0(\mathbf{r}',\mathbf{r},-i\tau)$$

格林函数采用原子轨道表象

$$G^0(\mathbf{r},\mathbf{r}',i\tau) = \sum_{i,j}\sum_{\mathbf{r},\mathbf{r}'}\varphi_i(\mathbf{r}-\mathbf{r})G_{i,j}(\mathbf{r}'-\mathbf{r},i\tau)\varphi_j(\mathbf{r}'-\mathbf{r}')$$

$$G_{i,j}(\mathbf{R},i\tau) = \begin{cases} -\dfrac{1}{N_{\mathbf{k}}}\displaystyle\sum_{n,\mathbf{k}} f_{n\mathbf{k}}c_{i,n}(\mathbf{k})c^*_{j,n}(\mathbf{k})e^{-\mathbf{k}\cdot\mathbf{r}}e^{-(\epsilon_{n,\mathbf{k}}-\mu)\tau} & \tau <= 0, \\ \dfrac{1}{N_{\mathbf{k}}}\displaystyle\sum_{n,\mathbf{k}}(1-f_{n\mathbf{k}})c_{i,n}(\mathbf{k})c^*_{j,n}(\mathbf{k})e^{-\mathbf{k}\cdot\mathbf{r}}e^{-(\epsilon_{n,\mathbf{k}}-\mu)\tau} & \tau > 0, \end{cases}$$

局域单位元分解技术(LRI)

$$\chi^0(r,r',i\tau) = \sum_{\mu,\nu,\mathbf{R},\mathbf{R}'} P_\mu(r-\mathbf{R})\chi^0_{\mu,\nu}(\mathbf{R}'-\mathbf{R},i\tau)P_\nu(r'-\mathbf{R}')$$

辅助基表象下的响应函数

$$\boxed{\chi^0_{\mu,\nu}(\mathbf{R},i\tau)} = -i\left[\sum_{i\in\mathcal{U}}\sum_{k,\mathbf{R}_1} C^{\mu(\mathbf{0})}_{i(\mathbf{0}),k(\mathbf{R}_1)}\left(M^\nu_{i,k}(\mathbf{R}_1,\mathbf{R},i\tau) + M^{\nu*}_{i,k}(\mathbf{R}_1,\mathbf{R},-i\tau)\right.\right.$$
$$\left.\left. + Z^\nu_{i,k}(\mathbf{R}_1,\mathbf{R},i\tau) + Z^{\nu*}_{i,k}(\mathbf{R}_1,\mathbf{R},-i\tau)\right)\right]$$

对称性化简

$$M^\nu_{i,k}(\mathbf{R}_1,\mathbf{R},i\tau) = \sum_{j\in\mathcal{V}} G_{i,j}(\mathbf{R},i\tau)N^\nu_{j,k}(\mathbf{R}_1,\mathbf{R},i\tau),$$

$$N^\nu_{j,k}(\mathbf{R}_1,\mathbf{R},i\tau) = \sum_{l,\mathbf{R}_2} C^{\nu(\mathbf{0})}_{j(\mathbf{0}),l(\mathbf{R}_2-\mathbf{R})}G_{l,k}(\mathbf{R}_1-\mathbf{R}_2,-i\tau),$$

$$Z^\nu_{i,k}(\mathbf{R}_1,\mathbf{R},i\tau) = \sum_{j\in\mathcal{V}} G_{j,k}(\mathbf{R}_1-\mathbf{R},-i\tau)X^\nu_{i,j}(\mathbf{R}_1,\mathbf{R},i\tau),$$

$$X^\nu_{i,j}(\mathbf{R},i\tau) = \sum_{l,\mathbf{R}_2} C^{\nu(\mathbf{0})}_{j(\mathbf{0}),l(\mathbf{R}_2-\mathbf{R})}G_{i,l}(\mathbf{R}_2,i\tau).$$

分配原子对计算 $\chi^0_{\mu,\nu}(\boldsymbol{R}, i\tau)$

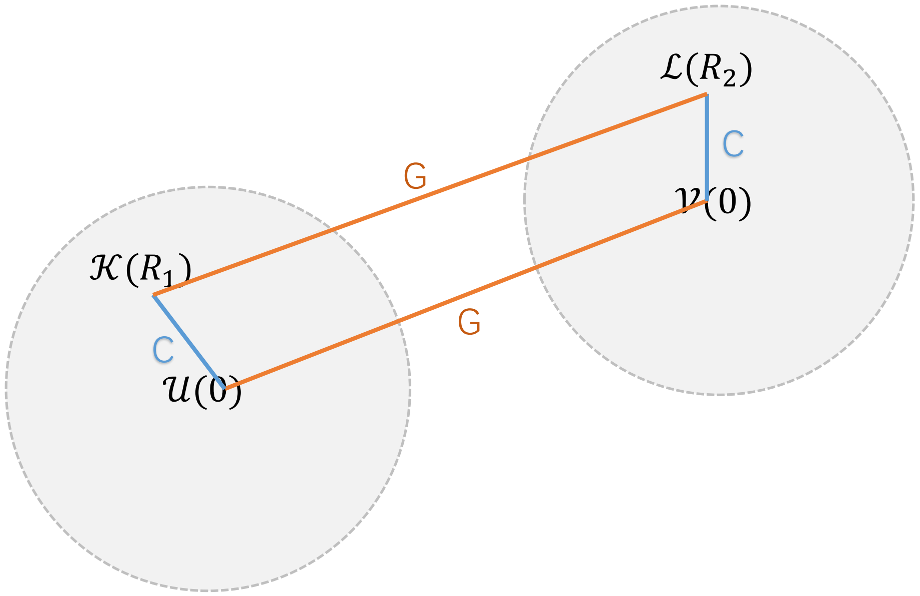
Algorithm 1 Loop structure based on $<\mathcal{U}(\mathbf{0}),\mathcal{V}(\mathbf{0})>$ atomic pairs

```
for all τ do
  for all R do
    for all <U(0),V(0)> do
      for all L(R2) ∈ N[V(0)] do
        Calculate X^ν_{i,j}(R1, R, iτ)
      end for
      for all K(R1) ∈ N[U(0)] do
        for all L(R2) ∈ N[V(0)] do
          Calculate N^ν_{j,k}(R1, R, iτ)
        end for
        Calculate M^ν_{i,k}(R1, R, iτ) , Z^ν_{i,k}(R1, R, iτ)
      end for
      Calculate temporary variable O_{μ,ν}[ U(0), V(0) ]
    end for
    Calculate χ^0_{μ,ν}(R, iτ)
  end for
end for
```

$G(R)$ 在实空间有局域性, 系统无限大时逼近 O(N)

原子对的数目随系统尺寸 O(N^2) 增长

LRI：与系统尺寸无关

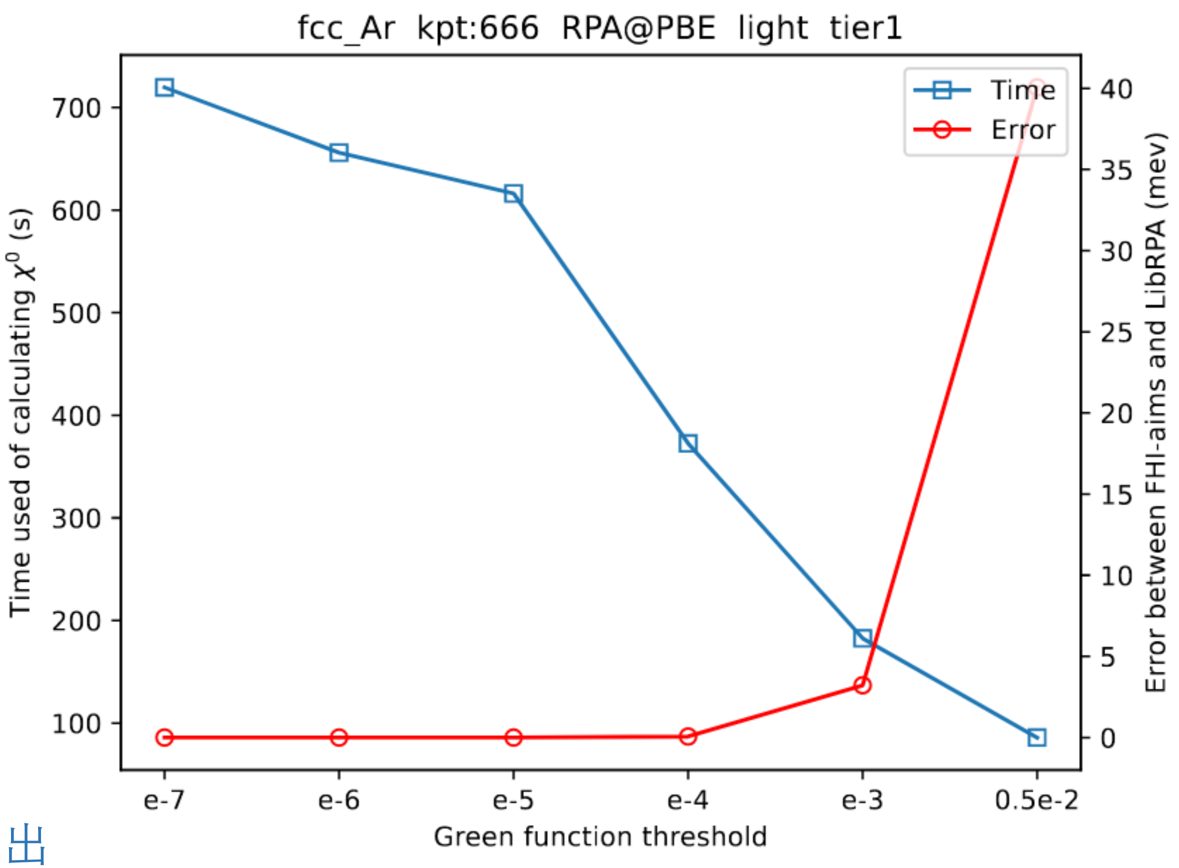


O(N)复杂度的探索

设置阈值，屏蔽无贡献的格林函数

Algorithm 2 Prescreening Green function $G_{i,j}(\mathbf{R}, i\tau)$

for all τ **do**
  for all $\mathbf{R}$ **do**
    for all $< \mathcal{U}(\mathbf{0}), \mathcal{V}(\mathbf{0}) >$ **do**
      if $max[Abs(G_{i,j}(\mathbf{R}, i\tau))\ matrix\ elements] \geq Threshold$ **then**
        Save $G_{i,j}(\mathbf{R}, i\tau)$
      else
        Discard $G_{i,j}(\mathbf{R}, i\tau)$
      end if
    end for
  end for
end for



减少格林函数将降低χ^0的计算时间，系统尺寸越大效果越突出

RPA关联能

$$G^0_{i,j}(\mathbf{R}, i\tau) \xrightarrow[\text{LRI}]{\text{CC}} \chi^0_{\mu,\nu}(\mathbf{R}, i\tau) \xrightarrow{\text{CT}} \chi^0_{\mu,\nu}(\mathbf{R}, i\omega) \xrightarrow{\text{FT}} \chi^0_{\mu,\nu}(\mathbf{q}, i\omega) \xrightarrow{\text{ACFDT}} E_c^{RPA}$$

$$\chi^0(\mathbf{r}, \mathbf{r}', i\tau) = -iG^0(\mathbf{r}, \mathbf{r}', i\tau)G^0(\mathbf{r}', \mathbf{r}, -i\tau)$$

Cosine变换 $$\chi^0_{\mu,\nu}(\mathbf{R}, i\omega_k) = \sum_{j=1}^{N} \gamma_{jk}\chi^0_{\mu,\nu}(\mathbf{R}, i\tau_j)\, cos(\tau_j\omega_k)$$ 使用Minimax格点完成时频转换

傅里叶变换 $$\chi^0_{\mu,\nu}(\mathbf{q}, i\omega) = \sum_{\mathbf{R}} e^{-i2\pi\mathbf{q}\mathbf{R}}\chi^0_{\mu,\nu}(\mathbf{R}, i\omega)$$

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

Kaltak M， Klime J， Kresse G . Low Scaling Algorithms for the Random Phase Approximation: Imaginary Time and Laplace Transformations

库仑奇异值的处理

辅助函数

$$\tilde{K}^{aux}_{\vec{G}} = \begin{cases} 4\pi/G^2, & \vec{G} \neq 0, \\ N_k \int_{\mathbf{BZ}} \frac{\Omega d\vec{k}}{(2\pi)^3} f(\vec{k}) - \sum_{\delta\vec{k}} f(\delta\vec{k}), & \vec{G} = 0. \end{cases}$$

$$f(q) = \frac{1}{1/(2\pi)^2} \Bigg\{ 4 \sum_{i=1}^{3} [b_j \sin(a_j \cdot q/2)] \cdot [b_j \sin(a_j \cdot q/2)] + 2 \sum_{i=1}^{3} [b_j \sin(a_j \cdot q)] \cdot [b_{j+1} \sin(a_{j+1} \cdot q)] \Bigg\}^{-1}.$$

修改库仑核

$$v^{sph} = (\mathbf{r}) = \begin{cases} \frac{1}{|\mathbf{r}|}, & if |\mathbf{r}| \leq R_c, \\ 0, & otherwise. \end{cases}$$

$$\tilde{K}^{sph}_{\vec{G}} = \int d\mathbf{r}\, e^{-i\vec{G}\cdot\vec{r}} \frac{1}{r} = \begin{cases} \frac{4\pi}{G^2}(1 - cos(\mathbf{G} \cdot \mathbf{R}_c)), & \vec{G} \neq 0, \\ 2\pi R_c^2, & \vec{G} = 0. \end{cases}$$

$$\frac{4\pi}{3} R_c^3 = \Omega$$

Wigner-Seitz原胞截断

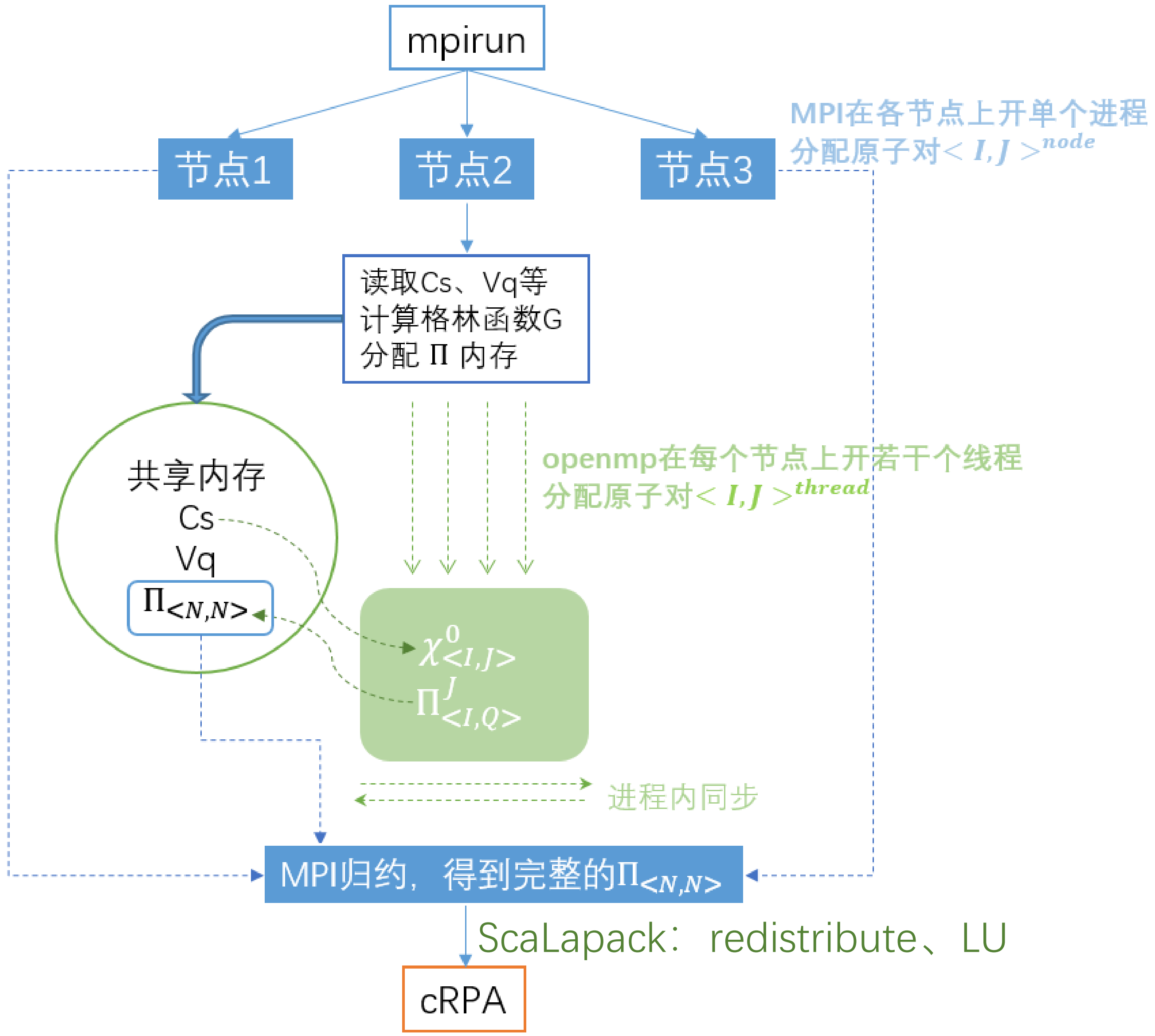
$$\tilde{K}^{WS}_{\vec{G}} = \int_{WS} d\vec{r}\, e^{-i\vec{G}\cdot\vec{r}} \left(\frac{erfc\ \alpha r}{r} + \frac{erf\ \alpha r}{r} \right) \approx \frac{4\pi}{G^2}\left(1 - exp\frac{-G^2}{4\alpha^2}\right) + \frac{\Omega}{N_{\vec{r}}} \sum_{\vec{r} \in WS} e^{-i\vec{G}\cdot\vec{r}} \frac{erf\ \alpha r}{r}.$$

Pierre, Carrier, Stefan, et al. General treatment of the singularities in Hartree-Fock and exact-exchange Kohn-Sham methods for solids

James, Spencer, Ali, et al. Efficient calculation of the exact exchange energy in periodic systems using a truncated Coulomb potential

Sundararaman R, Arias T A. Regularization of the Coulomb singularity in exact exchange by Wigner-Seitz truncated interactions: Towards chemical accuracy in nontrivial systems

并行方案：MPI+openmp



子任务分配方案：

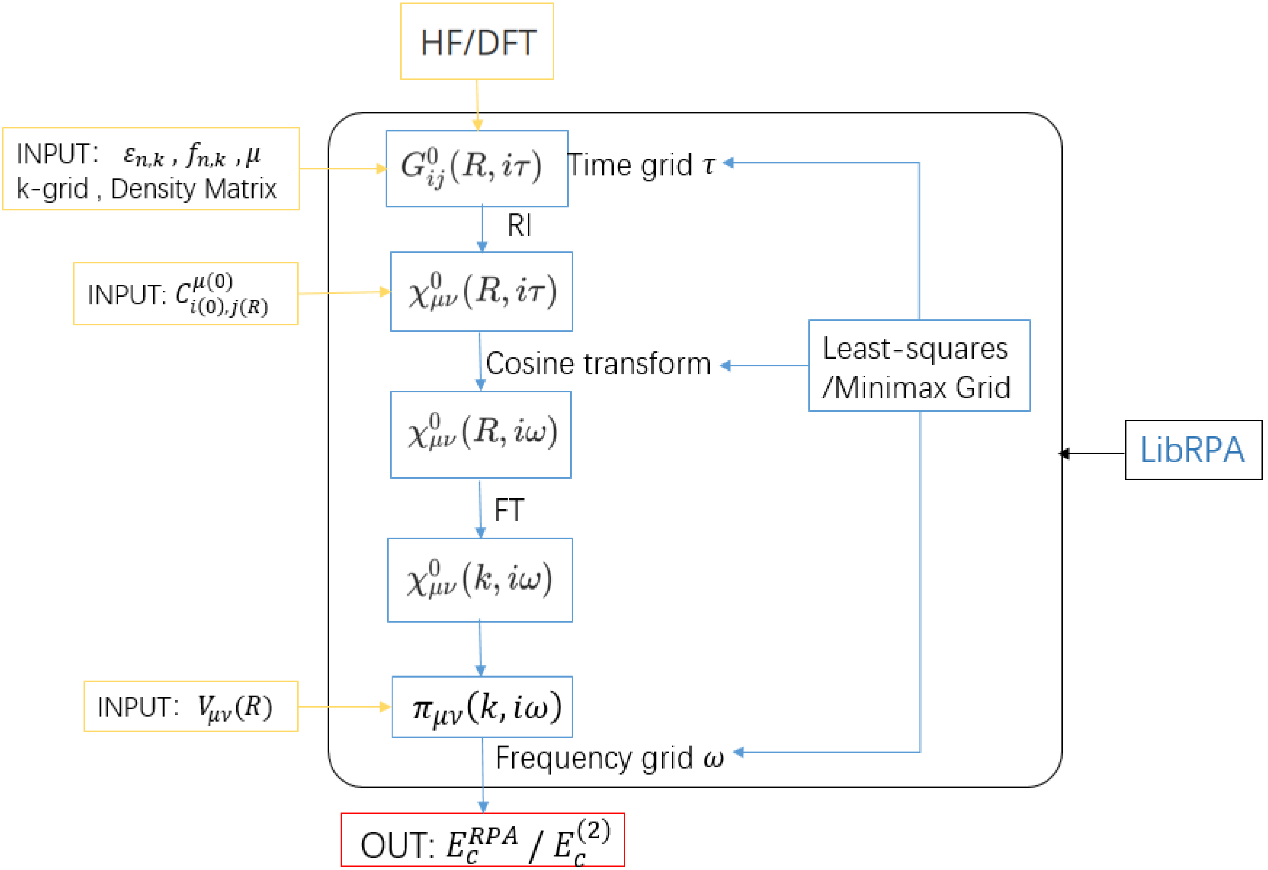
1. 原子对{<I,J>}
2. 时间格点与实空间格式{(R，τ)}

底层：

C++、Python

Lapack、ScaLapack

与FHI-aims的接口及结果比对



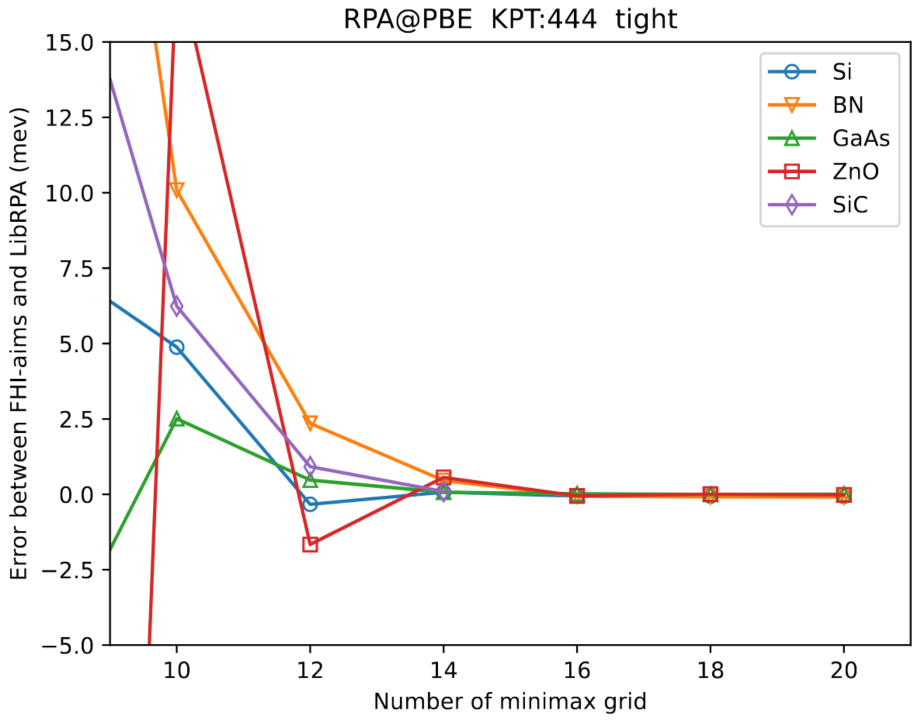
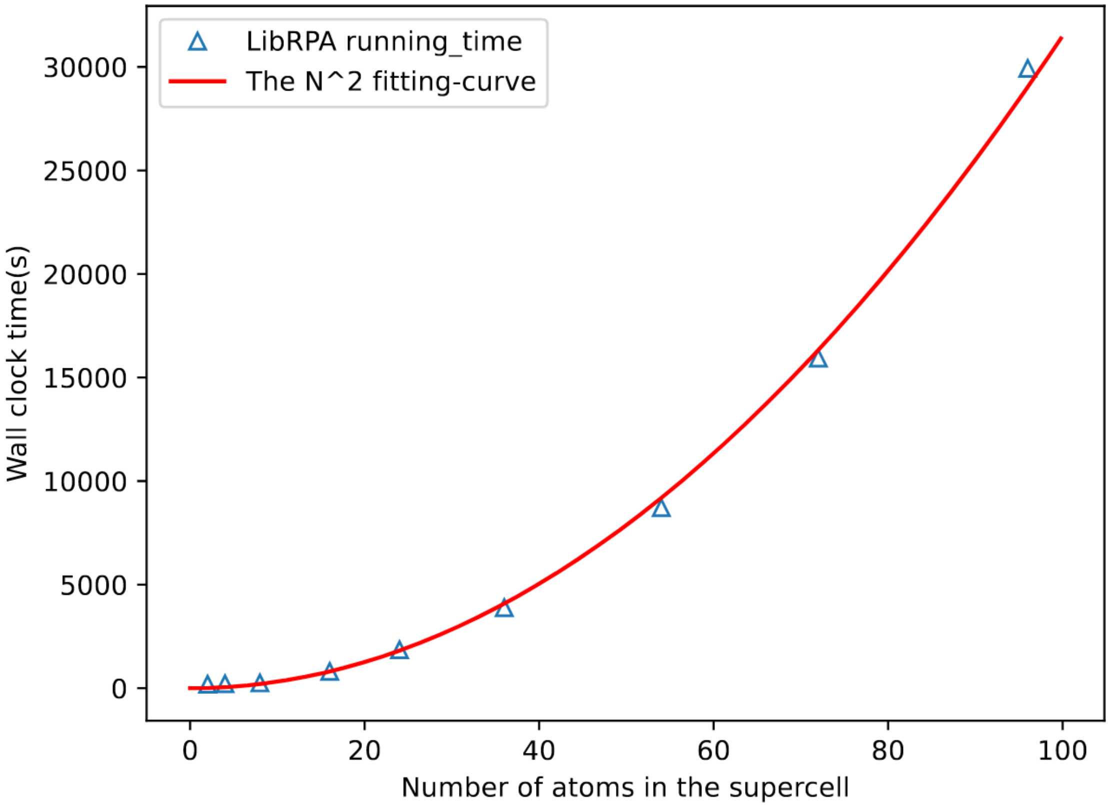


Figure 2: The RPA correlation energy errors between FHI-aims and LibRPA using different number of minimax grid. The results are obtained by RPA@PBE calculation using 4*4*4 k-points.

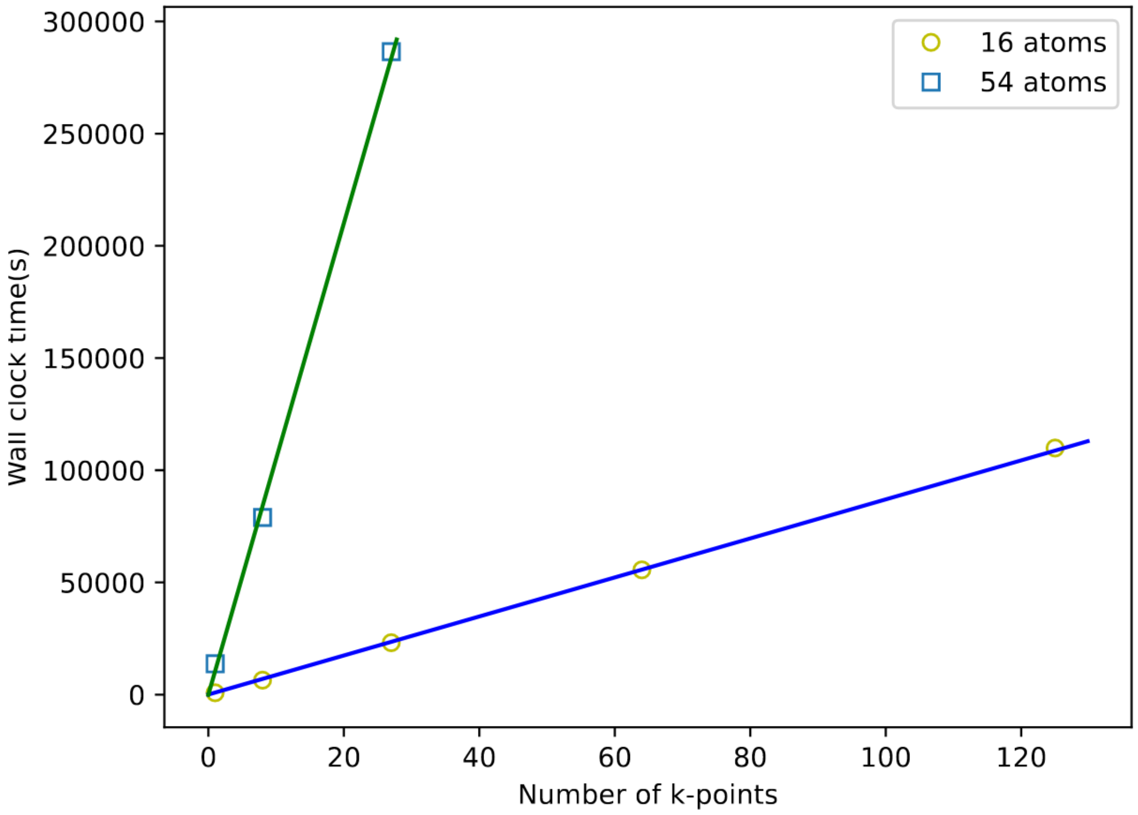
时间复杂度的验证

随系统尺寸平方增长



(a) Time used grows over the number of atoms

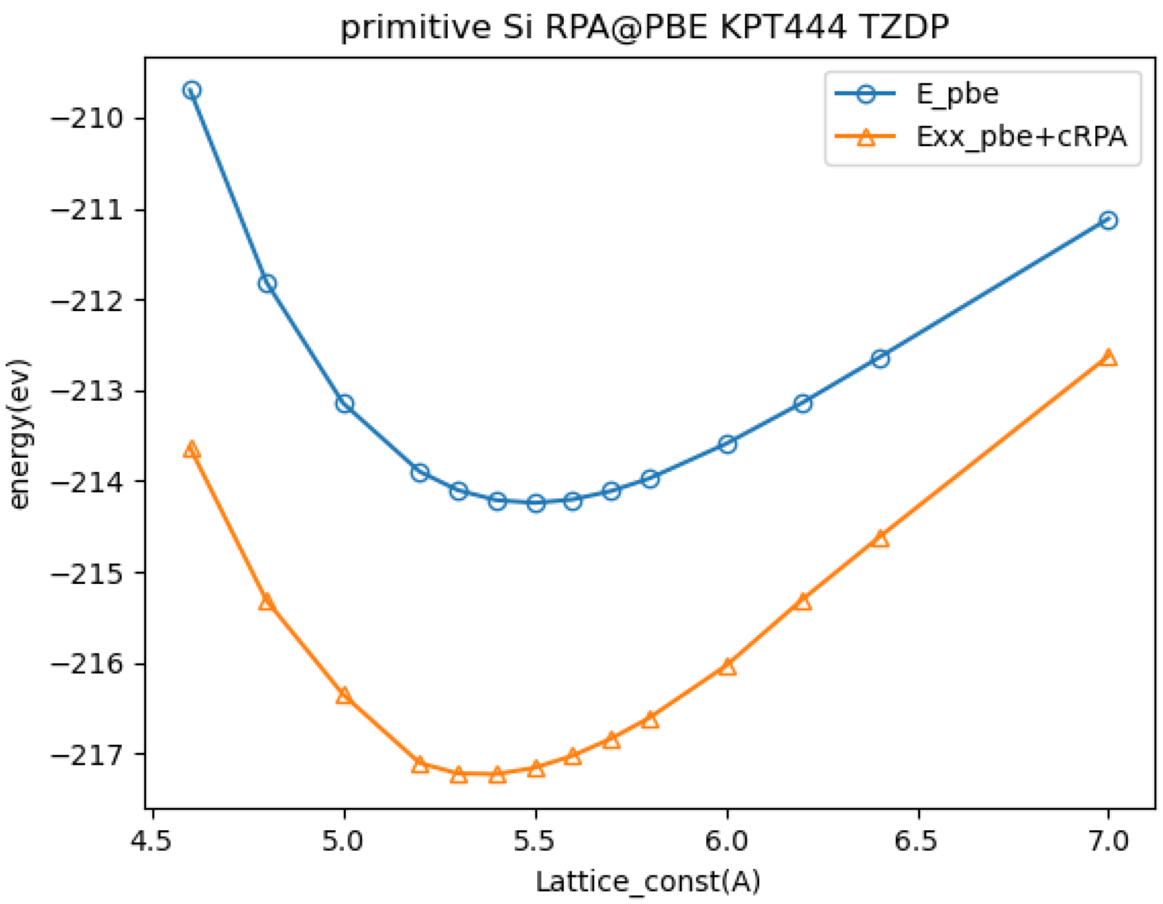
随k点数线性增长



(b) Time used grows over the number of k-points

与ABACUS的接口及结果测试

$$E^{EXX+RPA@PBE} = E_{PBE} - E_{xc} + E_X + E_c^{RPA}$$



ABACUS-LibRPA KPT:888 DZP error(%)

Lattice constants($\AA$)

	PBE	error	RPA	error	Expt.
C	3.5751	0.6	3.5535	0	3.553
SiC	4.3986	1	4.3722	0.6	4.346
Si	5.4789	1	5.3815	-0.7	5.421
GaAs	5.7836	2.5	5.4777	-2.9	5.640

Bulk Moduli(GPa)

	PBE	error	RPA	error	Expt.
C	420	-5	430	-3	443
SiC	209	-7	219	-3	225
Si	89	-10	108	9	99
GaAs	52	-31	81	6.6	76

总结

进展：

- 实现MPI+openmp混合并行
- 实现了与FHI-aims以及ABACUS的接口
- 使得ABACUS可以进行RPA@PBE计算
- 可靠的高精度结果
- 验证了$O(N^2)$ 的时间复杂度

展望：

- 进一步探索大规模体系中 O(N) 复杂度的算法
- 低标度GW方法的实现
- 在ABACUS中生成更适合于RPA的基组
- 依托于ABACUS的大规模体系的应用与研究
- 介电函数的计算（光谱、EELS）