Immersed Atom into Jellium Sphere

treated by CHAMP

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Goal

Inhomogeneity effects on \( \text{XC potentials} \)

Inverse Kohn-Sham scheme

Charge Density

DMC evaluation

As a simplest system...

Immersed Atom into Jellium Sphere
Background (1)

**Inverse Kohn-Sham Scheme**
Inverse KS scheme

In Principle,

\[ v_{XC}(\vec{r}) \] can be constructed so that it can reproduce \[ \rho(\vec{r}) \]

\[ \rho(\vec{r}) \] can be obtained by reliable treatment about electronic correlation

CI/DMC/ExactDiag.
Special Case ; 2-elec. systems

2-elec. Singlet systems (He atom)

Only the lowest orbital occupied...

\[ v_{XC}(\rho; \vec{r}) = \varepsilon_{KS} + \frac{1}{2} \frac{\nabla^2 \psi_{\text{lowest}}}{\psi_{\text{lowest}}} - v_{\text{ext}}(\vec{r}) - \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' \]

\[ \psi_{\text{lowest}}(\vec{r}) = \frac{\sqrt{\rho(\vec{r})}}{\sqrt{2}} \quad ; \text{(Closed-shell in a lowest orbital)} \]

\[ \varepsilon_{KS} = E_G + \frac{Z^2}{2} \quad ; \text{(KS-level equals to ionization energy)} \]

\( v_{XC}(\vec{r}) \) is obtained analytically, directory from \( \rho(\vec{r}) \) & \( E_G \)

evaluated by Hylleraas-type Variational calc.

Umrigar and Gonze, PRA50, 3827 (1994)
Comparison with LDA/GGA

Relying on such special relations (analytically feasible inverse KS)

- Umrigar and Gonze, PRA50, 3827 (1994)
More General way


Exploiting "Haydock-Foulkes" functional for Inverse Kohn-Sham

General/numerical feasibility

\[ V_0(\vec{r}) \text{; true potential to reproduce given } \rho_0(\vec{r}) \]

\[ V_{\text{Trial}}(\vec{r}) \text{; trial potential} \]

Upper bound property

\[ I[V_{\text{Trial}}(\vec{r}); \rho_0(\vec{r})] = -\sum_{iocc.} \epsilon_i [V_{\text{Trial}}(\vec{r})] + \int d^3 r V_{\text{Trial}}(\vec{r}) \rho_0(\vec{r}) \geq I[V_0(\vec{r}); \rho_0(\vec{r})] \]

Haydock-Foulkes Functional


How to get XC potential to reproduce a given \( \rho_0(\vec{r}) \) numerically?

Optimize \( V_{\text{Trial}}(\vec{r}) \) so that it may minimize \( I[V_{\text{Trial}}(\vec{r}); \rho_0(\vec{r})] \)

\( \rho_0(\vec{r}) \) evaluated by CI methods for Ne atom and methane molecule
Procedure

1. Provide DMC density \( \rho_0(\vec{r}) \)
2. Initial Guess of \( V(\vec{r}) \) by LDA
3. KS-SCF to get KS-level \( \{\varepsilon_j\} \) & \( \rho(\vec{r}) \)
4. Evaluate
   \[
   \mathcal{Y}[V] = - \sum_{i \text{occ}} \varepsilon_i[V] + \int V(\vec{r})\rho_0(\vec{r})d\vec{r}
   \]
5. \( |\rho(\vec{r}) - \rho_0(\vec{r})| < \delta \)?
   - Yes: Finish
   - No: Update \( V(\vec{r}) \) by Conjugate Gradient method
Background (2)

Immersed systems
Why interesting?

- Solid state theory
  
  Firstly modelled as Homogeneous Electron Gas

  Inhomogeneity effects due to ionic cores
  
  How it dominates for the origin of FCC/BCC structures?

  Energy gain by immersing atom into Jellium (Embedding Energy)

  Practical application of Embedding Energy --> Effective Medium Theory


- Electronic Structure theory

  Inhomogeneity effects on XC potential
Inverse Kohn-Sham
for immersed system

2-electrons in a sphere with and w/o background.

Exact diagonalization to get accurate densities

Then obtain XC potentials by Inverse Kohn-Sham.

Comparison with LYP, P91, PBE, PZ

Difference investigated
Setting up the Project
Project

- DMC calculation of a Immersed Atom into HEG to get Charge densities
- Inverse Kohn-Sham scheme using Haydock-Foulkes functional minimization to get XC potential $V_{XC}(r;Z,r_s)$

Immersed Atom into HEG
Localized basis Delocalized basis

Immersed Atom into Jellium Sphere.
Systems

Infinite Potential Wall

Jellium Sphere Background \((+N - Z)\)

nucleus \((+Z)\)

electrons \((-N)\)

Infinite Potential Wall is introduced for convergence reason

Specified by \((r_s,Z)\)
Procedure

Generate Trial Node by LDA

Trial/Guiding WaveFunction

QMC by CHAMP

DMC charge density

Inverse Kohn-Sham scheme

Exchange Correlation Potential
Jellium Sphere

without impurity (Z=0)

Several reference QMC works available upto N=106

Technical stuff

to be prepared

• **LDA generation of trial WF**

  Implementation of DFT for spherically symmetric systems
  (LDA part of PBE/Numerov method)

• **QMC calculation :**
  - High angular momentum (upto any $L$ by recursive generation)
  - Matrix operation with large size
    (General treatment for Multi-det. Sometimes fails)

• **Inverse Kohn-Sham scheme**

  Implemented by Conjugate Gradient method.

  ... Other extensions are quite straightforward.
Occupation
upto Higher angular momentum

(e.g., $Z=2$, $rs=5, 25$, $N=60$)

$1s(2)$
$2s(2) \ 1p(6)$
$3s(2) \ 2p(6) \ 1d(10)$
\[ \begin{array}{ccc}
** & ** & ** & 1f(14) \\
** & ** & ** & ** & 1g(18)
\end{array} \]

We follow the unfamiliar convention such as '1p' or '1d' as in

Results

(DMC charge density calc.)
**System treated**

(Simple Jellium sphere without impurity)

\[ Z = 0 \]
## Comparison with prev. work

(Z=0, N=106, rs=1.0/ without Infinite pot. wall)

<table>
<thead>
<tr>
<th>Energy (eV/electron.)</th>
<th>Std.err.</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.7965</td>
<td>-</td>
<td>LDA, S&amp;B</td>
</tr>
<tr>
<td>12.7987</td>
<td>-</td>
<td>LDA, present</td>
</tr>
<tr>
<td>12.8678</td>
<td>*</td>
<td>VMC, S&amp;B</td>
</tr>
<tr>
<td>12.8539</td>
<td>0.0047</td>
<td>VMC, present</td>
</tr>
<tr>
<td>12.8184</td>
<td>0.0043</td>
<td>DMC, S&amp;B</td>
</tr>
<tr>
<td>12.8158</td>
<td>0.0001</td>
<td>DMC, present</td>
</tr>
</tbody>
</table>

System treated
(with Infinite pot. wall)

\[ \begin{align*}
N &= 58 \\
N &= 60
\end{align*} \]
Densities

\(Z=2, \, rs=5.25, \, N=60\)

\[ 4\pi r^2 \rho(r) \]

\[ \rho(r) \]

\[ r(\text{a.u.}) \]

\[ r(\text{a.u.}) \]
Densities

$Z=2, \, rs=1.0, \, N=60$

$4\pi r^2 \rho(r)$
Densities

\[ Z = 2, \quad r_s = 3.0, \quad N = 60 \]

\[ 4\pi r^2 \rho(r) \]
Densities

$Z=2$, $r_s=5.25$, $N=60$

$4\pi r^2 \rho(r)$

$r(a\mu.)$
Results
(Inverse Kohn-Sham scheme)
Atomic Case (Be)

(Benchmark)

![Graph showing the comparison of different potential curves for Be, including Umrigar, Inverting KS, V_{xc-GGA}, V_{xc-LDA}, and -1/r. The graph plotting V_{xc} (Hartree) against r (Bohr).]
Atomic Case (Ne)

(Benchmark)

![Graph showing the behavior of various potentials with respect to distance for Ne.]

- **Umrigar**
- **Inverting KS with Scaling**
- **Inverting KS with Weak Scaling**
- **Inverting KS without Scaling**
- **$V_{xc}$-GGA**
- **$V_{xc}$-LDA**
- $-1/r$
Jellium Sphere ($z=0$)

$Z=0$. $rs=1$. $N=106$
Jellium Sphere \((z=2)\)

\(rs=5.25, N=60\)