Kohn-Sham calculations with “exact” exchange-correlation potential
Zhao-Morrison-Parr method (1)

**main idea**

1) Consider a system: \( N \) and \( v_{\text{ext}}(\mathbf{r}) \) (denoted as \( v_0(\mathbf{r}) \) here)

2) Solve accurately (Quantum Monte Carlo, CI, CCSD, for instance) the Schrödinger equation and obtain \( \rho_0 \)

3) Solve a modified Kohn-Sham equation:

\[
\left[ -\frac{1}{2} \nabla^2 + v_0(\mathbf{r}) + v_c^\lambda(\mathbf{r}) \right] \phi_i^\lambda(\mathbf{r}) = \epsilon_i^\lambda \phi_i^\lambda(\mathbf{r})
\]

where the term:

\[
v_c^\lambda(\mathbf{r}) = \lambda \int \frac{\rho(\mathbf{r'}) - \rho_0(\mathbf{r'})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r'}
\]

the additional constraint

\[
C[\rho, \rho_0] = \frac{1}{2} \int \int \frac{[\rho(\mathbf{r}) - \rho_0(\mathbf{r})][\rho(\mathbf{r'}) - \rho_0(\mathbf{r'})]}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r'} = 0
\]

The total Kohn-Sham potential for this system equals to \( v_0 + v_c^\lambda \).
Zhao-Morrison-Parr method (2) 
modification to assure correct asymptotic behavior

\[
\left[ -\frac{1}{2} \nabla^2 + v_0(\mathbf{r}) + \left( 1 - \frac{1}{N} \right) v_f^\lambda + v_c^\lambda(\mathbf{r}) \right] \phi_i^\lambda(\mathbf{r}) = \varepsilon_i^\lambda \phi_i^\lambda(\mathbf{r})
\]

The term (Fermi-Amaldi) 
\[v_f(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'\]
assures that the exchange-correlation potential calculated as:

\[v_{xc} = \lim_{\lambda \to \infty} \left( v_c^\lambda - \frac{1}{N} v_f^\lambda \right)\]

decays as \(-1/r\) far from nucleus in atomic systems.

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Zhao-Morrison-Parr method (3)
numerical verification of the “Janak theorem”

“Janak theorem:”

\[ I = -\varepsilon_{KS}^{\text{HOMO}} \]
for the exact exchange-correlation potential.

<table>
<thead>
<tr>
<th>Atom</th>
<th>( \varepsilon_{1s} )</th>
<th>( \varepsilon_{2s} )</th>
<th>( \varepsilon_{2p} )</th>
<th>( \varepsilon_{3s} )</th>
<th>( \varepsilon_{3p} )</th>
<th>(-I^a)</th>
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<tbody>
<tr>
<td>He</td>
<td>-0.9039</td>
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<td>Be</td>
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<tr>
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<td>-0.7923</td>
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<tr>
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<td>-11.11</td>
<td>-8.73</td>
<td>-1.07</td>
<td>-0.56</td>
<td>-0.5792</td>
</tr>
</tbody>
</table>

*From Ref. [10]. These values are inferred from experimental ionization potentials with all effects separated out that are not included in the nonrelativistic stationary-point-nucleus Schrödinger equation.
Zhao-Morrison-Parr method (4)
numerical values of $T[\rho]$, $T_s[\rho]$, and $T_c[\rho]$

$T_c[\rho]$ is one of the components of $E_{xc}[\rho]$. Is it numerically significant?

<table>
<thead>
<tr>
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<th>$T_s$</th>
<th>$T_c$</th>
<th>$T$</th>
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<tr>
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<tr>
<td>Ar</td>
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<td>0.71</td>
<td>527.37</td>
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</tbody>
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Zhao-Morrison-Parr method (5)
"exact" exchange-correlation potentials for atoms

\[ V_{xc} \]

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

He

Ar

Ne

Be

Fermi-Amaldi term


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Can Kohn-Sham equations be used for ground-states of multiconfigurational character?

from “exact” densities to the “exact” Kohn-Sham potential and the corresponding Kohn-Sham determinant

The construction of a non-interacting system (Kohn-Sham determinant and potential) yielding a given target densities (taken from high-level wavefunction based calculations) is possible using various techniques: ZMP (Zhao-Morrison-Parr), WY (Wu-Yang), and response based methods by Baerends et al.

Such techniques have been applied not only for interacting systems of essentially single-determinant ground state (H₂ at equilibrium geometry) but also for systems of a multi-determinantal character such as H₂ at large separations, H₂-H₂ at transition state, CH₂ at equilibrium geometry (Baerends et al).

Cases were also reported where such techniques failed: stretched CH₂, C₂ [Schipper et al, Theor. Chem. Acta (1998) 99, 329]. The current interpretation of such failures is that these are cases where the ground-state electron density is not “pure-state non-interacting v-representable”. 
Can Kohn-Sham equations be used for ground-states of multiconfigurational character?

A case study for dissociation of $H_2$ by Grüning et al.

$v_{xc}^{BB}(r)$ is a particular local potential in Kohn-Sham equations which describes correctly the dissociated system even if the true wavefunction is not a single determinant (stretched $H_2$).

$v_{xc}^{BB}(r)$ is a local potential but it depends explicitly not on density but on both occupied and unoccupied Kohn-Sham orbitals.

LDA, BP, are denote some simple approximations to $v_{xc}(r)$ (see latter). These approximations fail at large separations.

All results represent a spinless state of $H_2$.