



The origin of Optimised Effective Potential (OEP) Method

- The works of J.C Slater, R.T Sharp, G.K Horton, J. D. Talman, W. F. Shadwick, etc introduced the optimized effective potential schemes.
- In the Hartree Fock method each electron experiences a slightly different potential.
- J. C Slater proposed a method to solve the many-electron problem in a way that all electrons move in the same potential field[1] by incorporating a change in the Hartree Fock method.
- Slater constructed the averaged potential by performing the weighted mean of the exchange charges, weighted over the wave functions.
- Sharp and Horton formalized it as a variational problem and gave the expression for the form of potential that needs to be minimized.[2]
- Talman and Shadwick proposed the scheme to find the central potential of a many-electron system by variationally minimizing the potential with respect to energy.[3]
- Over the recent year many approaches toward OEP have been proposed by various researchers.

Why OEP

- There are a few advantages associated with the OEP schemes.
- The exchange-only OEP (OEPx) has a long history and possesses correct asymptotic behavior in the tail.
- The OEPx removes the one electron self-interaction error.
- OEPx is exact in the homogeneous electron gas limit.
- OEPx exhibits integer discontinuity upon addition of infinitesimal fraction of electron to the HOMO.
- OEPx obeys the exchange virial theorem.
- The OEP scheme is inevitable in Kohn - Sham DFT to find the exchange-correlation potential when the implicit density dependent functionals are employed.

General Formulation of OEP schemes

In the normal Kohn-Sham scheme, we find the true ground state density as equation (1) attains a minimum.

$$\frac{\delta E_{KS}[n_\downarrow, n_\uparrow]}{\delta n_\sigma(r)} \Bigg|_{n_\sigma=n_\sigma^0} = 0 \quad (1)$$

The exchange-correlation potential can be attained as below for functionals where their explicit dependence on the density is known

$$\frac{\delta E_{XC}[n_\downarrow, n_\uparrow]}{\delta n_\sigma(r)} \Bigg|_{n_\sigma=n_\sigma^0} = v_{xc}(r) \quad (2)$$

For functionals that explicitly depend on the orbitals, using equation (2) is not possible and the chain rule gives the following formula to obtain the exchange-correlation potential

$$v_{xc\sigma}(r) = \sum_{j=1}^{N_\sigma} \int d^3r' \left(\frac{\delta E_{xc}}{\delta \phi_{j\sigma}(r')} \frac{\delta \phi_{j\sigma}(r')}{\delta n_\sigma(r)} + c.c \right) \quad (3)$$

When the orbitals are functionals of the effective potential, we get

$$v_{xc\sigma}(r) = \sum_{j=1}^{N_\sigma} \int d^3r' \int d^3r'' \left(\frac{\delta E_{xc}}{\delta \phi_{j\sigma}(r')} \frac{\delta \phi_{j\sigma}(r')}{\delta v_{s\sigma}(r'')} + c.c \right) \frac{\delta v_{s\sigma}(r'')}{\delta n_\sigma(r)} \quad (4)$$

Equation (4) is the integral OEP equation that needs to be solved to find the exchange-correlation potential.

OEP in KS framework

The self-consistent KS equation is given by

$$\left[-\frac{1}{2} \nabla^2 + v_{s,\sigma}(\mathbf{r})[n] \right] \phi_{p\sigma}(\mathbf{r}) = \varepsilon_{p\sigma} \phi_{p\sigma}(\mathbf{r}) \quad (5)$$

where the local effective KS potential is given by

$$v_{s,\sigma}(\mathbf{r})[n] = v_{ext}(\mathbf{r}) + v_J(\mathbf{r}) + v_{xc,\sigma}(\mathbf{r}) \quad (6)$$

The electron density being

$$n(\mathbf{r}) = \sum_{\sigma} n_{\sigma}(\mathbf{r}) = \sum_{i,\sigma} |\phi_{i\sigma}(\mathbf{r})|^2 \quad (7)$$

The Hartree Fock exchange energy can be computed from

$$E_x[\{\phi_{q\tau}\}] = -\frac{1}{2} \sum_{\sigma} \sum_{ij} (i_{\sigma} j_{\sigma} | j_{\sigma} i_{\sigma}) \quad (8)$$

Correlated OEP

The correlation energy as described by the second-order OEP-GL2 method is

$$E_c^{(2)} = \frac{1}{2} \sum_{\sigma\tau} \sum_{ijab} \frac{|(i_{\sigma} a_{\sigma} | j_{\tau} b_{\tau})|^2}{\varepsilon_{i\sigma} + \varepsilon_{j\sigma} - \varepsilon_{a\tau} - \varepsilon_{b\tau}} - \frac{1}{2} \sum_{\sigma\tau} \sum_{ijab} \frac{(i_{\sigma} a_{\sigma} | j_{\tau\tau})(i_{\sigma} b_{\sigma} | j_{\tau} a_{\tau})}{\varepsilon_{i\sigma} + \varepsilon_{j\sigma} - \varepsilon_{a\tau} - \varepsilon_{b\tau}} + \sum_{\sigma} \sum_{ia} \frac{|f_{ia}^{\sigma}|^2}{\varepsilon_{i\sigma} - \varepsilon_{a\sigma}} \quad (9)$$

The OEP integral equation takes the form

$$\int X_{\sigma}(\mathbf{r}, \mathbf{r}') v_{xc,\sigma}^{OEP}(\mathbf{r}') d\mathbf{r}' = \Lambda_{xc}^{\sigma}(\mathbf{r}) \quad (10)$$

where

$$X_{\sigma}(\mathbf{r}, \mathbf{r}') = \sum_{pq} (\mathbf{X})_{pq}^{\sigma} g_p^*(\mathbf{r}) g_q(\mathbf{r}') \quad (11)$$

where

$$(\mathbf{X})_{pq}^{\sigma} = \int g_p^*(\mathbf{r}) X_{\sigma}(\mathbf{r}, \mathbf{r}') g_q(\mathbf{r}') d\mathbf{r}' d\mathbf{r} \\ = \sum_{ia} \left(\frac{(i_{\sigma} a_{\sigma} | p)(i_{\sigma} a_{\sigma} | q)^*}{\varepsilon_{i\sigma} - \varepsilon_{a\sigma}} + c.c. \right) \quad (12)$$

To ensure the correct asymptotic behavior in tail, the Fermi Amaldi potential can be added to the OEP exchange-correlation potential.

$$v_{xc,\sigma}^{OEP}(\mathbf{r}) = v_{Slater/FA}^{\sigma}(\mathbf{r}) + \sum_{p=1}^M c_p^{\sigma} g_p(\mathbf{r}) \quad (13)$$

Aim and Method

- The integral OEP equation in a finite basis set is an ill conditioned mathematical problem and regularization schemes are utilised to solve the integral OEP equations.
- The aim of the study is to clear the ambiguity involved in employing OEP in practice.
- All calculations were done in finite basis set LCAO basis using the ACES II package.
- We have studied different closed and open shell systems employing different basis set to study the convergence behavior of different OEP schemes such as OEPx, OEP2-sc, OEP-GL2.

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Convergence of He atom

Basis set	SVD=ON		SVD=OFF	
	FA	NONE	FA	NONE
OEPx				
cc-pVTZ	2.8612	0	0	diverge
cc-pVTZ/P1	2.8612	0	0	diverge
cc-pVTZ/P2	2.8612	0	0	diverge
aug-cc-pVQZ	2.8615	0	0	diverge
UGBS ¹	2.8617	0	0	diverge
20S10P2D	2.8617	0	0	diverge
OEP-GL2				
cc-pVTZ	2.9052	10^{-5}	diverge	diverge
cc-pVTZ/P1	2.9052	10^{-5}	diverge	diverge
cc-pVTZ/P2	2.9052	10^{-6}	diverge	diverge
aug-cc-pVQZ	2.9085	10^{-8}	diverge	diverge
UGBS	2.8801	10^{-9}	diverge	diverge
20S10P2D	2.9078	10^{-9}	diverge	diverge
OEP2-sc				
cc-pVTZ	2.8949	0	diverge	diverge
cc-pVTZ/P1	2.8949	0	diverge	diverge
cc-pVTZ/P2	2.8949	0	diverge	diverge
aug-cc-pVQZ	2.8976	0	diverge	diverge
UGBS	2.8752	0	diverge	diverge
20S10P2D	2.8970	0	diverge	diverge

*) the SVD cutoff was set to 10^{-6} ;

Total energies of different systems

Atom	OEP-GL2		OEPx	
	Numerical	LCAO	Numerical	LCAO
He	2.9099	2.9097	2.8617	2.8617
Li	7.4818	7.4805	7.4325	7.4325
Be	14.6965 ¹⁾	14.6948 ¹⁾	14.5724	14.5724
N	54.6216	54.6206	54.4034	54.4032
Ne	129.0265	129.0223	128.5454	128.5452
Na	162.3195	162.3081	161.8566	161.8564
Mg	200.1286	200.1190	199.6116	199.6115
P	341.3382	341.3300	340.7150	340.7150
Ar	527.6608	527.6515	526.8122	526.8121
ME[mHa]	-5.2153	ME[mHa]	-0.1000	
MAE[mHa]	5.2153	MAE[mHa]	0.1000	
MARE[%]	0.0063	MARE[%]	0.0002	

1) From perturbative calculation based on the OEPx density.

Conclusions

- Our study concludes that to obtain physically meaningful solutions using the OEP scheme, it is necessary to use appropriate regularization schemes, such as the truncated singular value decomposition along with the judicious choice of the basis set.
- We also show that we can avoid the variational collapse mentioned in certain literature through the above technique.
- We also found that using sufficiently large basis set helps in convergence and obtaining meaningful solutions.

References

- J. C Slater , Physical Review, **1951**, 81.
- R.T Sharp, G.K Horton,Physical Review **1953**,90.
- J. D Talman and W.F Shadwick, Physical Review A, **1976**, 14.
- Aditi Singh, Vignesh Balaji Kumar, Ireneusz Grabowski and Szymon Śmiga , Advances in Quantum Chemistry **2023**, 93.