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REGULAR ARTICLE

A variational density matrix approach with nonlocal effective potential

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Abstract We show that using the Colle–Salvetti correlation-energy functional (Colle and Salvetti in Theoret Chim Acta 37:329, 1975) in the Hartree–Fock-type procedure suggested by Kohn and Sham (Phys Rev 140:A1133PR, 1965), one can calculate quite accurately electronic properties of systems in which the “dynamical” correlation energy is dominant. We compare our results with those obtained by Grabo and Gross (Chem Phys Lett 240:141, 1995) using the optimized effective potential method, and we discuss characteristics and advantages of our procedure.

1 Introduction

About 30 years ago, Colle and Salvetti [1] (CS) proposed a method for approximating the correlation energy of a many-electron system starting from a pair-correlated Hartree–Fock (HF) wave function. The idea behind this proposal was that for a large number of atoms and molecules (at their equilibrium geometry) the correlation energy is dominated by its “dynamical“ component [2], that due to short-range pair correlations whose efficient representation requires the inclusion of interelectronic coordinates in the wave function. In these atomic and molecular systems, the spin-restricted Hartree–Fock wavefunction gives the best mean-field representation of the electronic state with the correct spin and symmetry properties, and the HF density is usually quite close to the true density. These facts, together with considerations based on the virial theorem [3], suggest that the correlation energy can be successfully approximated by correlating only the HF pair density, i.e. the diagonal term of the HF two-particle density matrix.

The pair-correlated wavefunction proposed by CS for the ground state of a closed shell N-electron system is the following

$$\Psi_{\mathrm{CS}}(x_1,\ldots,x_N) = \Psi_{\mathrm{HF}}(x_1,\ldots,x_N)\Pi_{i>j}[1-\varphi(\mathbf{r}_i,\mathbf{r}_j)] \tag{1}$$

where $\Psi_{\mathrm{HF}}(x_1,\ldots,x_N)$ is the single determinant HF wavefunction ($x_i \equiv \mathbf{r}_i\sigma_i$) and

$$\varphi(\mathbf{r}_1,\mathbf{r}_2) = \mathrm{e}^{-\beta^2(\mathbf{R})r^2}\left[1-\Phi(\mathbf{R})\left(1+\frac{r}{2}\right)\right] \tag{2}$$

is the correlation factor given as function of the center of mass $\mathbf{R} = (\mathbf{r}_1+\mathbf{r}_2)/2$ and relative position $r = |\mathbf{r}_1-\mathbf{r}_2|$ of an electron pair. In Eq. 2, $\Phi(\mathbf{R})$ gives the local strength of the Coulomb hole, the term linear in r takes care of the electronic cusp condition and, using the concept of Wigner exclusion volume [4, 5], the inverse radius of the correlation hole is chosen to be $\beta(\mathbf{R}) = q\rho_{\mathrm{HF}}^{1/3}(\mathbf{R})$ with $\rho_{\mathrm{HF}}(\mathbf{R})$ the HF density and $q = 2.29$ fitted to the helium atom.

Exploiting the Gaussian decrease of the correlation factor, CS approximate the spinless two-particle density matrix disregarding factors that involve the interaction of a given pair with the rest of electrons, thus obtaining

$$\begin{aligned} P_2(\mathbf{r}_1,\mathbf{r}_2;\mathbf{r}'_1,\mathbf{r}'_2) &= P_{2\mathrm{HF}}(\mathbf{r}_1,\mathbf{r}_2;\mathbf{r}'_1,\mathbf{r}'_2) \\ &\times\left[1-\varphi(\mathbf{r}_1,\mathbf{r}_2)-\varphi(\mathbf{r}'_1,\mathbf{r}'_2)+\varphi(\mathbf{r}_1,\mathbf{r}_2)\varphi(\mathbf{r}'_1,\mathbf{r}'_2)\right] \end{aligned} \tag{3}$$

The function $\Phi(\mathbf{R})$ in Eq. 2 is determined by enforcing the identity of the CS one-particle density matrix with the HF one:

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$$P_{1\mathrm{CS}}(\mathbf{r}_1,\mathbf{r}'_1) = \frac{1}{N-1}\int d\mathbf{r}_2 P_{2\mathrm{CS}}(\mathbf{r}_1,\mathbf{r}_2;\mathbf{r}'_1,\mathbf{r}_2) = P_{1\mathrm{HF}}(\mathbf{r}_1,\mathbf{r}'_1) \tag{4}$$

An approximate solution of the above integral equation, obtained by CS only for the diagonal elements of the density matrices, is $\Phi(\mathbf{R}) = \sqrt{\pi}\beta(\mathbf{R})/[1+\sqrt{\pi}\beta(\mathbf{R})]$. Note that, since Eq. 4 has not been solved for the out-diagonal elements of the density matrices, the use of Ψ_{CS} with the above expression of $\Phi(\mathbf{R})$ is not justified in actual calculations [6, 7].

Constrain (4) guarantees the normalization of Ψ_{CS}, gives $\rho_{\mathrm{CS}}(\mathbf{r}) = \rho_{\mathrm{HF}}(\mathbf{r})$ and satisfies the sum rule for the density of the exchange-correlation hole:

$$\int d\mathbf{r}_2 \rho_{\mathrm{CS}}(\mathbf{r}_2)[g_{\mathrm{CS}}(\mathbf{r}_1,\mathbf{r}_2) - 1] = -1 \tag{5}$$

where $g_{\mathrm{CS}}(\mathbf{r}_1,\mathbf{r}_2)$ is the pair-distribution function defined in terms of the CS pair density:

$$g_{\mathrm{CS}}(\mathbf{r}_1,\mathbf{r}_2) = \frac{P_{2\mathrm{CS}}(\mathbf{r}_1,\mathbf{r}_2)}{\rho_{\mathrm{CS}}(\mathbf{r}_1)\rho_{\mathrm{CS}}(\mathbf{r}_2)} = \frac{P_{2\mathrm{HF}}(\mathbf{r}_1,\mathbf{r}_2)}{\rho_{\mathrm{HF}}(\mathbf{r}_1)\rho_{\mathrm{HF}}(\mathbf{r}_2)}[1-\varphi(\mathbf{r}_1,\mathbf{r}_2)]^2 \tag{6}$$

Owing to constraint (Eq. 4), the correlation energy in CS approximation is simply given by

$$\begin{aligned} E_c^{\mathrm{CS}} &= \langle\Psi_{\mathrm{CS}}|\hat{H}|\Psi_{\mathrm{CS}}\rangle - \langle\Psi_{\mathrm{HF}}|\hat{H}|\Psi_{\mathrm{HF}}\rangle \\ &= \frac{1}{2}\int d\mathbf{r}_1 \int d\mathbf{r}_2 P_{2\mathrm{HF}}(\mathbf{r}_1,\mathbf{r}_2)\frac{[\varphi^2(\mathbf{r}_1,\mathbf{r}_2) - 2\varphi(\mathbf{r}_1,\mathbf{r}_2]}{|\mathbf{r}_1-\mathbf{r}_2|} \\ &= \frac{1}{2}\int d\mathbf{R} \int d\mathbf{r} P_{2\mathrm{HF}}(\mathbf{R},\mathbf{r})\frac{[\varphi^2(\mathbf{R},\mathbf{r}) - 2\varphi(\mathbf{R},\mathbf{r}]}{r} \end{aligned} \tag{7}$$

This expression has been further simplified by CS replacing the correlation energy per electron (as resulting from the **r**-integration of Eq. 7) with a four parameters function that fits accurately the exact function in the range of densities relevant to the helium atom:

$$\begin{aligned} E_c^{\mathrm{CS}} &= \frac{1}{2}\int d\mathbf{R} P_{2\mathrm{HF}}(\mathbf{R},\mathbf{R})\frac{4\pi}{\rho_{\mathrm{HF}}(\mathbf{R})}H[\beta(\mathbf{R}),W(\mathbf{R})] \\ H(\beta,W) &= -0.01565\frac{1+0.173We^{-0.58/\beta}}{1+\frac{0.8}{\beta}}; \\ W(\mathbf{R}) &= \frac{1}{\beta^2(\mathbf{R})}\left[\frac{\Delta_{\mathbf{r}}P_{2\mathrm{HF}}(\mathbf{R}-\mathbf{r}/2,\mathbf{R}+\mathbf{r}/2)}{P_{2\mathrm{HF}}(\mathbf{R}-\mathbf{r}/2,\mathbf{R}+\mathbf{r}/2)}\right]_{\mathbf{r}=0} \end{aligned} \tag{8}$$

The functional form of $H(\beta,W)$ has been suggested by the expansion of $P_{2\mathrm{HF}}(\mathbf{r}_1,\mathbf{r}_2)$ to second order about $\mathbf{r}=0$, followed by integration with respect to **r** of Eq. 7. The low-density damping factor $e^{(-0.58/\beta)}$ has been introduced to recover the Wigner functional form of the correlation energy per electron in the low-density limit of a uniform electron gas [4, 8]. Note that, owing to this factor, the CS correlation energy functional (Eq. 8) is better performing on the uniform electron gas (see [9]) than Eq. 7 or its second order approximation (Eq. 15 of [1]).

Finally, we point out that the CS correlation energy is a functional of the HF one-particle density matrix because of $W(\mathbf{R})$ in which

$$\Delta_{\mathbf{r}}P_{2\mathrm{HF}}(\mathbf{r}_1,\mathbf{r}_2)\Big|_{\mathbf{r}_1=\mathbf{r}_2=\mathbf{R}} = \rho_{\mathrm{HF}}(\mathbf{R}) \times\left[\frac{1}{4}\Delta\rho_{\mathrm{HF}}(\mathbf{R}) - \frac{1}{2}\frac{|\nabla\rho_{HF}(\mathbf{R})|^2}{\rho_{\mathrm{HF}}(\mathbf{R})} + \nabla_1\nabla_2 P_{1\mathrm{HF}}(\mathbf{r}_1,\mathbf{r}_2)\Big|_{\mathbf{r}_1=\mathbf{r}_2=\mathbf{R}}\right]. \tag{9}$$

2 A variational approach

The central result of the CS procedure [1, 10] is the total electronic energy of a closed shell system given as an explicit functional of the one-particle density matrix obtained from a single-determinant (SD) wavefunction:

$$\begin{aligned} E[P_{1\mathrm{SD}}] &= \left[\int d\mathbf{r}\left(-\frac{1}{2}\Delta_{\mathbf{r}} + v_{\mathrm{en}}(\mathbf{r}) + \frac{1}{2}\int d\mathbf{r}_2\frac{\rho_{\mathrm{SD}}(\mathbf{r}_2)}{|\mathbf{r}-\mathbf{r}_2|}\right) \times P_{1\mathrm{SD}}(\mathbf{r},\mathbf{r}')|_{\mathbf{r}'=\mathbf{r}} + E_x[P_{1\mathrm{SD}}]\right] \\ &\quad + E_c^{\mathrm{CS}}[P_{1\mathrm{SD}}] = E_{\mathrm{SD}}[P_{1\mathrm{SD}}] + E_c^{\mathrm{CS}}[P_{1\mathrm{SD}}] \\ E_x[P_{1\mathrm{SD}}] &= -\frac{1}{4}\int d\mathbf{r}\int d\mathbf{r}'\frac{|P_{1\mathrm{SD}}(\mathbf{r},\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|}; \\ E_c^{\mathrm{CS}}[P_{1\mathrm{SD}}] &= \pi\int d\mathbf{R}\rho_{\mathrm{SD}}(\mathbf{R})H[\beta,W(\mathbf{R})] \end{aligned} \tag{10}$$

with $H[\beta(\mathbf{R}), W(\mathbf{R})]$ defined in terms of $P_{1\mathrm{SD}}$. Because of the orbital structure of $P_{1\mathrm{SD}}(\mathbf{r},\mathbf{r}') = 2\Sigma_{j=1}^{N/2}\psi_j^*(\mathbf{r}')\psi_j(\mathbf{r})$, the ground state energy $E[P_{1\mathrm{SD}}\{\psi_j\}]$ is a functional of the $N/2$ lowest eigenfunctions of the Hartree–Fock operator modified by a local correlation potential:

$$\begin{aligned} &\left[-\frac{1}{2}\Delta_{\mathbf{r}} + v_{\mathrm{en}}(\mathbf{r}) + \int d\mathbf{r}'\frac{\rho_{\mathrm{SD}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + v_c(\mathbf{r})\right]\psi_j(\mathbf{r}) \\ &\quad -\frac{1}{2}\int d\mathbf{r}'\frac{P_{1\mathrm{SD}}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\psi_j(\mathbf{r}') = \epsilon_j\psi_j(\mathbf{r}) \\ &[F_{\mathrm{HF}}(\mathbf{r}) + v_c(\mathbf{r})]\psi_i(\mathbf{r}) = \epsilon_i\psi(\mathbf{r}); \quad v_c(\mathbf{r}) = \frac{\delta E_c^{\mathrm{CS}}[P_{1\mathrm{SD}}]}{\delta P_{1\mathrm{SD}}(\mathbf{r},\mathbf{r}')}\Big|_{\mathbf{r}'=\mathbf{r}}. \end{aligned} \tag{11}$$

Note that this system of equations is formally identical to that discussed by Kohn and Sham (KS) in Sec. IIB of [11] where, however, the correlation potential is the functional derivative of the correlation energy with respect to the density and not to the density matrix as in Eq. 11. More recently, the orbital energy functional $E[P_{1\mathrm{SD}}\{\psi_j\}]$ defined in Eq. 10 for closed shells has been utilized by Grabo and Gross (GG) [12] in the context of the optimized effective potential (OEP) method

[13, 14]. The orbitals are obtained from the solution of a single-particle Schrödinger equation with a local effective potential determined by the condition that its orbitals be the ones that minimize the energy functional:

$$[-\frac{1}{2}\Delta_{\mathbf{r}} + V_{\mathrm{OEP}}(\mathbf{r})]\psi_j(\mathbf{r}) = \epsilon_j\psi_j(\mathbf{r}); \quad \frac{\delta E[P_{1\mathrm{SD}}\{\psi_j\}]}{\delta V_{\mathrm{OEP}}(\mathbf{r})} = 0 \tag{12}$$

Since the solution of the integral equation required by the OEP method is numerically very involved, GG have utilized the KLI approximation [15, 16] of the OEP equation obtaining more accurate results than with the conventional KS method. In the next section, we show that our variational approach gives slightly better or equivalent results than the GG procedure without requiring, however, the solution of OEP (or KLI) equations, and with a numerical effort equivalent to that of a standard HF calculation.

The CS procedure can be naturally extended to treat open shell states (e.g. excited states orthogonal by symmetry to the ground state) whose independent particle representation requires a single-configuration (SC) wavefunction linear combination of several determinants with fixed symmetry coefficients. In these cases, the CS expression for the total electronic energy is a functional of the spin-reduced two-particle density matrix $P_{2\mathrm{SC}}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}_2)$ obtained from the SC wavefunction:

$$\begin{aligned} E[P_{2\mathrm{SC}}\{\psi_\alpha, \psi_\beta\}] = {} & \left[\int \mathrm{d}\mathbf{r}\left(-\frac{1}{2}\Delta_{\mathbf{r}} + v_{\mathrm{en}}(\mathbf{r})\right)P_{1\mathrm{SC}}(\mathbf{r}, \mathbf{r}')|_{\mathbf{r}'=\mathbf{r}} \right. \\ & \left. + \frac{1}{2}\int \mathrm{d}\mathbf{r}\int \mathrm{d}\mathbf{r}' \frac{P_{2\mathrm{SC}}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\right] \\ & + \frac{1}{2}\int \mathrm{d}\mathbf{R}\, P_{2\mathrm{SC}}(\mathbf{R}, \mathbf{R})\frac{4\pi}{\rho_{\mathrm{SC}}(\mathbf{R})}H[\beta(\mathbf{R}), W(\mathbf{R})] \\ & = E_{\mathrm{SC}}[P_{2\mathrm{SC}}\{\psi_\alpha, \psi_\beta\}] + E_c^{\mathrm{CS}}[P_{2\mathrm{SC}}\{\psi_\alpha, \psi_\beta\}] \end{aligned} \tag{13}$$

with $H[\beta(\mathbf{R}), W(\mathbf{R})]$ defined in terms of $P_{2\mathrm{SD}}$. Since the two-particle density matrix can be expressed in terms of the α-spin $\{\psi_\alpha\}$ and β-spin $\{\psi_\beta\}$ orbitals of the SC wavefunction, the $E[P_{2\mathrm{SC}}]$ energy functional is an orbital energy functional $E[P_{2\mathrm{SC}}\{\psi_\alpha, \psi_\beta\}]$. The orbitals are solutions of the coupled single-particle equations characteristic of the specific open shell state, in which the generalized Hartree–Fock–Roothaan operators [17] are modified by a local correlation potential:

$$\begin{aligned} \frac{\delta E[P_{2\mathrm{SC}}\{\psi_\alpha, \psi_\beta\}]}{\delta\psi_i^*(\mathbf{r})} = {} & \frac{\delta E_{\mathrm{SC}}[P_{2\mathrm{SC}}\{\psi_\alpha, \psi_\beta\}]}{\delta\psi_i^*(\mathbf{r})} \\ & + \frac{\delta E_c^{\mathrm{CS}}[P_{2\mathrm{SC}}\{\psi_\alpha, \psi_\beta\}]}{\delta\psi_i^*(\mathbf{r})} \\ = {} & \Sigma_j \epsilon_{ij}\psi_j(\mathbf{r}). \end{aligned} \tag{14}$$

3 Results

To test the CS variational procedure (CSV) that utilizes Eqs. 10, 11 with $P_{1\mathrm{SC}}$ obtained from a restricted HF wavefunction for closed shell systems, and Eqs. 13, 14 with $P_{2\mathrm{SC}}$ obtained from a HF wavefunction for open shell systems, we have calculated the ground-state energy of first-row and second-row atoms. These energies are compared with estimates of the exact nonrelativistic values obtained from experimental ionization energies [18] and with accurate CI calculations [19] for first-row atoms, and with Lamb-shift corrected experimental values [12] for second-row atoms. These results are reported in Table 1 together with those obtained in [12] using the OEP-GG procedure and conventional KS method with two standard exchange-correlation functionals: BLYP [20, 21] and PW91 [22, 23]. Note that our calculations have been performed using standard basis sets of Gaussian functions that give the HF energies reported in the first column of Table 1.

Table 1 Total absolute ground-state energies (a.u.) of first-row and second-row atoms from various SCF calculations: HF, CSV; OEP-GG, KS-BLYP and KS-PW91 from [12]

Atom	HF	CSV	GG	BLYP	PW91	CI	Exact
He	2.8617	2.9033	2.9033	2.9071	2.9000	2.9049	2.9037
Li	7.4327	7.4845	7.4829	7.4827	7.4742	7.4743	7.4781
Be	14.5730	14.6660	14.6651	14.6615	14.6479	14.6657	14.6674
B	24.5291	24.6546	24.6564	24.6485	24.6299	24.6515	24.6539
F	99.4094	99.7296	99.7302	99.7581	99.7316	99.7268	99.734
Ne	128.5471	128.9225	128.9202	128.9730	128.9466	128.9277	128.939
$\overline{\Delta}$	0.1705	0.0050	0.0054	0.0129	0.0102	0.0046	
Na	161.8589	162.260	162.256	162.293	162.265	–	162.257
Mg	199.6146	200.066	200.062	200.093	200.060	–	200.059
Al	241.8767	242.364	242.362	242.380	242.350	–	242.356
Cl	459.4821	460.170	460.164	460.165	460.147	–	460.196
Ar	526.8175	527.560	527.553	527.551	527.539	–	527.604
$\overline{\Delta}$	0.5165	0.018	0.019	0.036	0.026	–	

The CI values are taken from [19], the exact nonrelativistic values (Exact) from [18] for the first-row atoms and from [12] for the second-row atoms. $\overline{\Delta}$ denotes the mean absolute deviation from the exact nonrelativistic values

Table 2 Ionization potentials (a.u.) of first-row and second-row neutral atoms from ground-state-energy differences calculated with CSV and taken from [12] for OEP-GG, KS-BLYP and KS-PW91

Atom	CSV	OEP-GG	KS-BLYP	KS-PW91	CI	Expt
He	0.903	0.903	0.912	–	0.905	0.903
Li	0.204	0.203	0.203	0.207	0.198	0.198
Be	0.327	0.330	0.330	0.333	0.344	0.343
B	0.311	0.314	0.309	0.314	0.304	0.305
F	0.623	0.621	0.656	0.660	0.639	0.640
Ne	0.769	0.767	0.808	0.812	0.792	0.792
$\overline{\Delta}$	0.011	0.012	0.010	0.014	0.001	
Na	0.193	0.191	0.197	0.198	–	0.189
Mg	0.273	0.275	0.280	0.281	–	0.281
Al	0.217	0.218	0.212	0.221	–	0.220
Cl	0.472	0.471	0.476	0.482	–	0.477
Ar	0.577	0.575	0.576	0.583	–	0.579
$\overline{\Delta}$	0.004	0.004	0.004	0.004		

The CI values are taken from [19], the experimental values (Expt) from [24]. $\overline{\Delta}$ denotes the mean absolute deviation from the experimental values

Table 3 Electron affinities (a.u.) from ground-state-energy differences of neutral first-row and second-row atoms calculated with CSV and taken from [12] for OEP-GG

Atom	CSV	OEP-GG	CI	Expt
Li	0.015	0.016	0.023	0.023
F	0.084	0.082	0.125	0.125
Na	0.014	0.015	–	0.020
Cl	0.124	0.122	–	0.133

The CI values are taken from [19], the experimental values (Expt) from [24]

Looking at the mean absolute errors reported in Table 1, we see that the CSV procedure is significantly more accurate than KS-BLYP and KS-PW91, slightly more accurate than the OEP-GG procedure and gives results nearly as accurate as the CI energies for the first row atoms.

In Table 2, we report the ionization potentials of first-row and second-row atoms calculated from ground-state-energy differences using the CSV procedure, and taken from [12] for the OEP-GG, KS-BLYP, KS-PW91 procedures. These results are compared with CI values taken from [19] and with experimental values from [24]. We see that the performance of CSV and OEP-GG is almost equivalent and comparable to that of the conventional KS methods in which, however, error cancelations between exchange and correlation energy can be relevant. The CI results for the first-row atoms are clearly more accurate, but the performance of CSV, OEP-GG and KS procedures is really impressive for the second-row atoms.

Table 4 Excitation energies (eV) of the first optically allowed transition in neutral first-row and second-row atoms calculated using the CSV procedure and compared with experimental values (see http://physics.nist.gov/PhysRefData/ASD/)

Atom	CSV	Expt
Li ($^2S \rightarrow {}^2P$)	1.88	1.85
B ($^2P \rightarrow {}^2S$)	5.22	4.96
Na ($^2S \rightarrow {}^2P$)	2.15	2.10
Cl ($^2P \rightarrow {}^2S$)	3.18	3.15

In Table 3, we compare electron affinities calculated from ground-state-energy differences using CSV and OEP-GG procedures, with the corresponding CI values taken from [19] and with experimental values from [24]. We see that the quality of the results obtained with CSV and OEP-GG is about the same, but appreciably lower than that of the CI results for first-row atoms. KS-BLYP and KS-PW91 electron affinities have not been reported in Table 3 since these procedures typically do not converge for negative ions.

Finally, in Table 4, we compare excitation energies of the first optically allowed transition in neutral first-row and second-row atoms calculated using the CSV procedure and compared with experimental values. We see that the performance of the CSV method is quite satisfactory with errors lower than 5% of the experimental value.

4 Conclusions

We have presented a variational procedure in which the total energy of a many-electron system is a functional of the two-particle density matrix obtained from the single-configuration wavefunction appropriate to the state of the system, and the correlation energy is the CS correlation energy functional [1]. The total electronic energy is an explicit functional of the orbitals which define the two-particle density matrix. The orbitals are obtained from the solution of single-particle Schrödinger equations with HF-type operators modified by a local correlation potential that is the functional derivative of the CS correlation energy.

This variational approach can be applied to closed and open shell states that can be properly described by a single-configuration wavefunction. The CSV procedure can be efficiently implemented with the same computational effort as a HF calculation, and gives total electronic energies significantly more accurate than those obtained using the conventional KS method with standard exchange-correlation functionals. Comparisons with results obtained using the OEP-KS method [12] show a similar degree of accuracy. The CSV procedure, however, seems easier to be efficiently implemented and more general since it can be applied to open-shall states (e.g. excited states) that cannot be represented by a single determinant wavefunction.

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