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ORIGINAL PAPER

Assessment of the March-Santamaria kinetic energy pair-density functional

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Abstract The quality of the March-Santamaria kinetic energy function for the spin-resolved electron pair density is assessed. While the March-Santamaria functional is exact for all pair densities that arise from a single Slater determinant wavefunction, its value tends to decrease (instead of increase) with increase correlation.

Keywords Kinetic energy · Pair density functional · March-Santamaria formula

1 Motivation

One way to construct a hierarchy of density-functional theories that is analogous to the Hartree-Fock, configuration interaction-singles CIS, CISD, CISDT,… hierarchy of traditional wavefunction-based ab initio theory is to consider the k-electron density as the fundamental descriptor of electronic systems [1,2]. In the limit as k approaches the number of electrons, exact results are obtained; this is reminiscent of the convergence of wavefunction-based ab initio methods to the exact result in the full-CI (where N-electron excitations are included) limit. We call methods based on the k-electron distribution function k-density functional theories.

Most work in k-density functional theory (k-DFT) has been focused on the electron pair density [3,4], but most of the work has been formal in nature, with few practical theoretical results. There seem to be two major obstacles to practical k-DFT approaches. The first is N-representability problem: for $k > 1$, some seemingly reasonable k-electron distribution function are unattainable by any N-fermion system [5]. While exact and approximate N-representability constraints are known, imposing

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these constraints on the variational principle is not easy.[2,6–10] For more information about the N-representability problem, the reader is referred to the review article by Davidson [11].

The other problem is that there is not simple, explicit, and accurate formula for the kinetic energy in terms of the k-electron density for $k < N$. Much of the previous work has been focused on the generalized Weizsäcker functionals [1,12–16] but, as shown in the companion paper, the accuracy of this functional is inadequate [17]. Just as with the N-representability problem, exact approaches to the kinetic-energy functional problem are known at a formal level [1,4,18,19], but these results are not practically useful. It is interesting that appropriately constructed kinetic-energy functionals can *include the N-representability* constraints [18–20]. Therefore, if a sufficiently accurate kinetic energy functional were known, the N-representability problem might be avoided.

Even before the rise of 2-density functional theory, March and Santamaria proposed a functional for the kinetic energy in terms of the same-spin electron pair density [21],

$$\begin{aligned}&\rho_2^{\sigma\sigma}\left(\mathbf{R}_1,\mathbf{R}_2\right)\\&\quad=\left\langle\Psi\left|\sum_{i_1\neq i_2}\left|\sigma\left(i_1\right)\sigma\left(i_2\right)\right\rangle\left(\delta\left(\mathbf{r}_{i_1}-\mathbf{R}_1\right)\delta\left(\mathbf{r}_{i_2}-\mathbf{R}_2\right)\right)\left\langle\sigma_2\left(i_2\right)\sigma\left(i_1\right)\right|\right|\Psi\right\rangle\end{aligned} \tag{1}$$

namely,

$$T_{\mathrm{MS}}=\sum_{\sigma=\alpha,\beta}\frac{-1}{8}\int\int\frac{\left|\nabla_1\left(\rho_2^{\sigma\sigma}\left(\mathbf{r}_1,\mathbf{r}_2\right)-\rho^{\sigma}\left(\mathbf{r}_1\right)\rho^{\sigma}\left(\mathbf{r}_2\right)\right)\right|^2}{\left(\rho_2^{\sigma\sigma}\left(\mathbf{r}_1,\mathbf{r}_2\right)-\rho^{\sigma}\left(\mathbf{r}_1\right)\rho^{\sigma}\left(\mathbf{r}_2\right)\right)}d\mathbf{r}_1d\mathbf{r}_2. \tag{2}$$

Here $\rho^{\sigma}(\mathbf{r})$ is the usual spin-resolved electron density. The March-Santamaria functional is derived for pair densities that arise from Slater determinants,

$$\rho_2^{\sigma\sigma}\ \left(\mathbf{r}_1,\mathbf{r}_2\right)=\gamma^{\sigma}\ \left(\mathbf{r}_1,\mathbf{r}_2\right)\wedge\gamma^{\sigma}\ \left(\mathbf{r}_1,\mathbf{r}_2\right), \tag{3}$$

and is exact in that case. The March-Santamaria functional may be derived as the lowest-order approximate kinetic energy functional that can be constructed from the cumulant expansion of the reduced density matrix (this gives Eq. (3)) [1]; in this sense it is conceptually similar to coupled-cluster theory [22–24].

The purpose of this article is to assess the accuracy of the March-Santamaria functional for spin-resolved pair densities. Because the March-Santamaria functional is based on the ansatz in Eq. (3), we use this approximation to the pair density, but we use correlated (not Slater determinant) density matrices. Presuming that the cumulant contribution (which is assumed to be zero in the derivation of the March-Santamaria functional) is negligible these results can reveal how good, or bad, the March-Santamaria functional is. Our basic finding in sect 3 is that the quality of the March-Santamaria functionals rapidly deteriorates as the quality of the pair density improves. Indeed, as electron correlation is introduced into a system, the kinetic energy should rise, but the March-Santamaria functional predicts the opposite trend.

2 Computational methods

The spin-resolved 2-densities (Eq. 1) were computed using the GAMESS program [25,26]. Hartree-Fock and complete active space self-consistent field (CASSCF) calculations were performed for different active spaces, approaching the full-CI limit. In order to keep the computational cost modest (accurately evaluating the integral in Eq. (2) is difficult), we used a small (3-21G) basis set. Our results are reported in Tables 1 and 2.

Table 1 Results from the March-Santamaria kinetic functional, T_{MS} for atoms and various active spaces (cf. 2)

Atom	$(K_{\text{core}}, N_{\text{active}}, K_{\text{active}})$	E_c	T	$\check{T}_{\text{MS}}$	Absolute error
He	HF	–	2.836	–	–
	(0, 2, 2)	−0.0149	2.859	2.821	0.0377
Li	HF	–	7.371	–	–
	(0, 3, 9)	−0.0003	7.369	7.369	0.0003
Be	HF	–	14.478	–	–
	(0, 4, 3)	−0.0024	14.478	14.472	0.0060
	(0, 4, 4)	−0.0189	14.486	14.392	0.0941
	(0, 4, 6)	−0.0327	14.494	14.349	0.1454
	(0, 4, 9)	−0.0446	14.500	14.321	0.1791
	(1, 2, 2)	−0.0023	14.478	14.472	0.0061
	(1, 2, 4)	−0.0188	14.488	14.395	0.0926
B	HF	–	24.315	–	–
	(0, 5, 3)	0	24.315	24.315	0
	(0, 5, 4)	−0.0177	24.329	24.217	0.1113
	(0, 5, 5)	−0.0329	24.341	24.154	0.1871
	(1, 3, 3)	−0.0176	24.328	24.217	0.1116
	(1, 3, 4)	−0.0328	24.341	24.154	0.1871
C	HF	–	37.351	–	–
	(0, 6, 4)	0	37.351	37.351	0
	(0, 6, 5)	−0.0181	37.364	37.239	0.1256
	(1, 4, 4)	−0.0181	37.364	37.239	0.1256
	(1, 4, 6)	−0.0217	37.369	37.228	0.1401
N	HF	–	53.918	–	–
	(0, 7, 5)	0	53.918	53.918	0
	(0, 7, 6)	−0.0011	53.919	53.917	0.0014
	(0, 7, 7)	−0.0048	53.923	53.906	0.0165
	(1, 5, 5)	−0.0009	53.919	53.918	0.0015
	(2, 3, 5)	−0.0037	53.922	53.907	0.0151
O	HF	–	74.149	–	–
	(0, 8, 5)	0	74.149	74.149	0
	(0, 8, 6)	−0.0004	74.151	74.149	0.0015

Table 1 continued

Atom	$(K_{\text{core}}, N_{\text{active}}, K_{\text{active}})$	E_c	T	$\check{T}_{\text{MS}}$	Absolute error
	(0, 8, 7)	−0.0095	74.161	74.123	0.0389
	(0, 8, 8)	−0.0170	74.173	74.107	0.0651
	(1, 6, 6)	−0.0096	74.162	74.162	0.0389
	(2, 4, 4)	−0.0092	74.161	74.121	0.0395
	(2, 5, 4)	−0.0179	74.172	74.101	0.0713
F	HF	–	98.537	–	–
	(0, 9, 5)	0	98.537	98.537	0
	(0, 9, 7)	−0.0186	98.559	98.485	0.0751
	(0, 9, 9)	−0.0319	98.576	98.463	0.1133
	(1, 7, 5)	−0.0013	98.539	98.537	0.0031
	(1, 7, 6)	−0.0101	98.549	98.507	0.0423
	(1, 7, 7)	−0.0328	98.576	98.457	0.1196
	(2, 5, 4)	−0.0097	98.551	98.509	0.0425
	(2, 5, 5)	−0.0188	98.561	98.485	0.0754
Ne	HF	–	127.418	–	–
	(0, 10, 6)	−0.0105	127.429	127.385	0.0442
	(0, 10, 7)	−0.0376	127.457	127.310	0.1472
	(0, 10, 8)	−0.0772	127.494	127.216	0.2777
	(0, 10, 9)	−0.1152	127.518	127.128	0.3902
	(1, 8, 5)	−0.0104	127.429	127.386	0.0435
	(1, 8, 6)	−0.0375	127.458	127.311	0.1468
	(1, 8, 7)	−0.0770	127.495	127.217	0.2776
	(1, 8, 8)	−0.1136	127.526	127.135	0.391
	(2, 6, 4)	−0.0100	127.429	127.386	0.0437
	(2, 6, 5)	−0.0367	127.458	127.301	0.1571
	(2, 6, 6)	−0.0758	127.495	127.219	0.2761
	(2, 6, 7)	−0.0774	127.498	127.217	0.2811

Active spaces are denoted as $(K_{\text{core}}, N_{\text{active}}, K_{\text{active}})$, where K_{core} is the number of occupied core orbitals, N_{active} is the number of electrons in the active space, and K_{active} is the number of orbitals in the active space. The kinetic energy is denoted T and the correlation energy is denoted $E_c = E_{(K_{\text{core}},N_{\text{active}},K_{\text{active}})} - E_{\text{HF}}$ and the kinetic energy is denoted T. All energies are reported in Hartree. The March-Santamaria functional is exact for the Hartree-Fock calculations

3 Assessing the March-Santamaria functional

Table 1 reports the results for the March-Santamaria functional for Helium and the second-row atoms, Li–Ne, for a variety of different active spaces. Exact results are obtained for Hartree-Fock (and are not reported); as the amount of electron correlation energy recovered increases, the true kinetic energy tends to increase, but the March-Santamaria approximation to the kinetic energy tends to decrease. The trend is wrong, but the results are much more accurate than we observed for the generalized-Weizsäcker functionals [17]. Nonetheless, errors of tens, and even hundreds, of milliHartree are routinely observed. This is much more accurate than many

Table 2 Results from the March-Santamaria kinetic functional, T_{MS} for the Beryllium isoelectronic series

Atom	$(K_{\mathrm{core}}, N_{\mathrm{active}}, K_{\mathrm{active}})$	E_c	T	$\check{T}_{\mathrm{MS}}$	Absolute error
Be	HF	–	14.478	–	–
	(0, 4, 3)	−0.0024	14.478	14.472	0.0060
	(0, 4, 4)	−0.0189	14.486	14.392	0.0941
	(0, 4, 6)	−0.0327	14.494	14.349	0.1454
	(0, 4, 9)	−0.0446	14.500	14.321	0.1791
	(1, 2, 2)	−0.0023	14.478	14.472	0.0061
	(1, 2, 4)	−0.0188	14.488	14.395	0.0926
B^+	HF	–	23.879	–	–
	(0, 4, 3)	−0.0025	23.874	23.867	0.0069
	(0, 4, 4)	−0.0234	23.901	23.738	0.1625
	(0, 4, 6)	−0.0413	23.922	23.661	0.2604
	(0, 4, 9)	−0.0569	23.938	23.610	0.3282
	(1, 2, 3)	−0.0234	23.902	23.739	0.1628
C^{2+}	HF	–	35.721	–	–
	(0, 4, 3)	−0.0023	35.715	35.709	0.0066
	(0, 4, 4)	−0.0284	35.755	35.496	0.2597
	(0, 4, 6)	−0.0506	35.786	35.365	0.4217
	(0, 4, 9)	−0.0702	35.811	35.276	0.5347
	(1, 2, 3)	−0.0282	35.749	35.483	0.2671
N^{3+}	HF	–	49.991	–	–
	(0, 4, 3)	−0.0022	49.984	49.978	0.0064
	(0, 4, 4)	−0.0335	50.038	49.654	0.3847
	(0, 4, 6)	−0.06	50.079	49.449	0.6303
	(0, 4, 9)	−0.0836	50.112	49.313	0.7990
	(1, 2, 3)	−0.0325	50.009	49.673	0.3360
	(1, 2, 4)	−0.0334	50.046	49.603	0.4429
O^{4+}	HF	–	66.799	–	–
	(0, 4, 3)	−0.0022	66.792	66.786	0.0059
	(0, 4, 4)	−0.0037	66.798	66.256	0.5420
	(0, 4, 9)	−0.0975	66.952	65.816	1.1357
	(1, 2, 3)	−0.0022	66.792	66.785	0.0068
F^{5+}	HF	–	86.020	–	–
	(0, 4, 3)	−0.0021	86.011	86.005	0.0066
	(0, 4, 4)	−0.0444	86.091	85.351	0.7405
	(0, 4, 6)	−0.0801	86.154	84.940	1.2133
	(0, 4, 9)	−0.1116	86.202	84.663	1.5395
	(1, 2, 3)	−0.0002	86.018	86.018	0
Ne^{6+}	HF	–	107.669	–	–
	(0, 4, 3)	−0.0021	107.660	107.653	0.0072

Table 2 continued

Atom	$(K_{\mathrm{core}}, N_{\mathrm{active}}, K_{\mathrm{active}})$	E_c	T	$\breve{T}_{\mathrm{MS}}$	Absolute error
	(0, 4,4)	−0.0501	107.752	106.782	0.9705
	(0, 4, 6)	−0.0907	107.823	106.237	1.5865
	(0, 4, 9)	−0.1262	107.880	105.867	2.0133
	(1, 2, 3)	−0.0003	107.667	107.667	−0.0001
Mg^{8+}	HF	–	152.082	–	–
	(0, 4, 3)	−0.0354	152.072	151.562	0.5100
	(0, 4, 6)	−0.0968	152.061	150.837	1.2244
	(1, 2, 3)	−0.0354	152.072	152.019	0.0530
	(1, 2, 4)	−0.0967	152.105	150.837	1.2242
Si^{10+}	HF	–	212.077	–	–
	(0, 4, 3)	0	212.077	212.077	0
	(0, 4, 6)	−0.1278	212.065	209.915	2.1504
	(1, 2, 3)	−0.0209	212.105	212.056	0.0494
	(1, 2, 4)	−0.1276	212.066	209.912	2.1537
	(1, 2, 8)	−0.1276	212.057	209.900	2.1570

The column headings have the same meaning as in Table 1

orbital-free kinetic energy density functionals, but still woefully inadequate for chemical applications.

The exact kinetic energy would *always* increase if the virial theorem held exactly (because reducing the energy by including electron correlation increases the kinetic energy), but the virial theorem is far from satisfied in this small basis. Still, the trend is clearly explained by the virial theorem.

Why is the March-Santamaria kinetic energy below the true kinetic energy? Why does it become worse when the amount of electron correlation decreases? Consider the cumulant expansion of the 2-electron reduced density matrix,

$$\Gamma_2 = \gamma \wedge \gamma + \Delta_2, \tag{4}$$

where Γ_2 is the 2-electron reduced density matrix and Δ_2 is the 2-electron reduced density cumulant. The second term is neglected in this paper and in the derivation of the March-Santamaria functional. The present approximation, then, reduces to

$$\breve{T}_{\mathrm{MS}} = \frac{1}{2}\int\int \nabla_1\gamma\left(\mathbf{r}_1, \mathbf{r}_2\right) \cdot \nabla_1\gamma\left(\mathbf{r}_2, \mathbf{r}_1\right) d\mathbf{r}_1 d\mathbf{r}_2 \approx T_{\mathrm{MS}} \tag{5}$$

Inserting the natural orbital expansion of the 1-electron reduced density matrix,

$$\gamma\left(\mathbf{r}_1, \mathbf{r}_2\right) = \sum_i n_i \chi_i\left(\mathbf{r}_1\right) \chi_i^*\left(\mathbf{r}_2\right) \quad 0 \le n_i \le 1 \tag{6}$$

into the right-hand-side of this equation gives

$$\begin{aligned}\breve{T}_{\mathrm{MS}} &= \frac{1}{2}\sum_i\sum_j n_i n_j \left(\int \nabla\chi_i(\mathbf{r}_1)\cdot\nabla\chi_j^*(\mathbf{r}_1)\,d\mathbf{r}_1\right)\left(\int \chi_i^*(\mathbf{r}_2)\,\chi_j(\mathbf{r}_2)\,d\mathbf{r}_2\right)\\ &= \frac{1}{2}\sum_i\sum_j n_i n_j \left(\int \nabla\chi_i(\mathbf{r}_1)\cdot\nabla\chi_j^*(\mathbf{r}_1)\,d\mathbf{r}_1\right)\delta_{ij}\\ &= \sum_i n_i^2\left(\frac{1}{2}\int \nabla\chi_i(\mathbf{r}_1)\cdot\nabla\chi_i^*(\mathbf{r}_1)\,d\mathbf{r}_1\right) \qquad (7)\end{aligned}$$

This can be compared to the exact result,

$$T = \sum_i n_i\left(\frac{1}{2}\int \nabla\chi_i(\mathbf{r}_1)\cdot\nabla\chi_i^*(\mathbf{r}_1)\,d\mathbf{r}_1\right) \qquad (8)$$

which differs only in that the natural orbital occupation numbers are not squared. Since the occupation numbers are between zero and one, $n_i^2 \leq n_i$, with equality only when $n_i = 0$ or $n_i = 1$. So the March-Santamaria functional is exact for an idempotent density matrix (corresponding to a Slater determinant) but in other cases the first contribution in Eq. (7) is below the true energy. The cumulant term should be negligible for the calculations used here: the dominant kinetic-energy contribution from the cumulant should be from the electron–electron cusp, which is poorly resolved in small basis sets like the ones used here.

To verify this reasoning, we considered the Beryllium isoelectronic series (Table 2). As the atomic number increases, the $2p$ and $2s$ orbitals become nearly degenerate, and the natural orbital occupation numbers for the $2p$ and $2s$ orbitals deviate further from their Hartree-Fock values of zero and one, respectively. So if the preceding explanation of the flaws in the March-Santamaria functional is correct, then we expect the quality of the approximation to deteriorate with increasing nuclear charge in Table 2. This is what is observed.

4 Summary

The March-Santamaria functional is exact for Hartree-Fock theory, but it gives results that are sometimes a few tenths of an a.u. too small when the pair density is approximated using correlated one-electron density matrices instead of the idempotent density matrices associated with Slater determinants. These results can be explained by noting the contribution of a single natural orbital to the kinetic energy is multiplied by the natural orbital occupation number in the exact theory, but by the square of the occupation number in the March-Santamaria approximation to it. We predict, based on this result, that the March-Santamaria functional may be useful for systems where the exact wavefunction is very close to Hartree-Fock (so that there is very little electron correlation), but such systems are unlikely to be especially important from a chemical point of view, so we did not pursue that line of reasoning further. The fact that the March-Santamaria functional tends to give kinetic energies that decrease with increasing electron correlation, while the true kinetic energy increases with increasing electron correlation, strongly suggests that a different approach to the pair-density kinetic-energy functional problem is needed.

Where do we go from here? The negative result in this paper and the previous one [17] suggests that it may be very difficult to derive a simple and explicit form of the kinetic energy functional for the pair density. The approach of Ayers and Levy [27], where the 2-density is only used to compute the correlation component of the kinetic energy, can ensure that the kinetic energy increases as electron correlation increases. This approach would, at least, solve the largest shortcoming of the March-Santamaria functional. Another possibility is to explicitly use a more sophisticated approximation to the underlying wavefunction in pair-density functional theory (thereby providing a better model for the treatment of non-integer occupation numbers), in the manner of Higuchi and Higuchi [28,29]. Finally, it would be interesting to validate this paper's assessment of the March-Santamaria functional using more accurate computations.

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