Chapter 17
Kinetic Energy Density Functionals from Models for the One-Electron Reduced Density Matrix

D. Chakraborty, R. Cuevas-Saavedra and P. W. Ayers

Abstract Orbital-free kinetic energy functionals can be constructed by writing the one-electron reduced density matrix as an approximate functional of the ground-state electron density. In order to utilize this strategy, one needs to impose appropriate N-representability constraints upon the model 1-electron reduced density matrix. We present several constraints of this sort here, the most powerful of which is based upon the March-Santamaria identity for the local kinetic energy.

17.1 Introduction

Practical density-functional theory (DFT) calculations use either the orbital-free method or the Kohn–Sham approach [1]. The orbital-free approach, in which the kinetic energy is directly approximated as an explicit functional of the electron density came first historically, and was a very popular approach through the mid-1980s. However, explicit kinetic energy functionals tend to have poor accuracy, and in particular are subject to variational collapse to chemically absurd solutions with energies that are far too low. This is often attributed to the difficulty of satisfying the Pauli principle using an explicit density functional [2–6], and motivates the idea of using an auxiliary function to evaluate the kinetic energy. Most commonly, one introduces the Kohn–Sham orbitals, which are functionals of the electron density constructed based on the requirement that the energy of the noninteracting Kohn–Sham reference system has the same electron density as the total system. The energy of the noninteracting system is then used a proxy for the energy of the true interacting system, with the remaining correlation-kinetic energy lumped into the exchange-correlation energy functional.

Despite its ubiquity, there is still interest in the orbital-free method, primarily because it is less computationally costly [7–12]. The key obstacle, clearly, is approximating the kinetic energy [7, 9, 10, 13–18] or, alternatively, its functional derivative

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[19–27]. It has been realized that effective calculations are usually nonlocal functionals of the electron density, which motivates introducing new auxiliary quantities like the 1-electron reduced density matrix, the exchange hole, or the linear response function [10–12, 18, 28–42].

Recently, we have proposed a strategy based on writing the 1-electron reduced density matrix as an explicit, nonlocal, functional of the electron density [43]. The exact Levy constrained search functional for the noninteracting (Kohn–Sham) kinetic energy of σ-spin electrons can be expressed in this way [44–46]

$$T_s^\sigma[\rho] = \min_{\{\gamma^\sigma:\, \rho^\sigma(\mathbf{r})=\gamma^\sigma(\mathbf{r},\mathbf{r}),\, \gamma^\sigma=(\gamma^\sigma)^2\}} \int\int \delta(\mathbf{r}-\mathbf{r}')\left(-\frac{1}{2}\nabla_{\mathbf{r}}^2\gamma^\sigma(\mathbf{r},\mathbf{r}')\right) d^3\mathbf{r}d^3\mathbf{r}', \tag{17.1a}$$

$$\gamma_s^\sigma[\rho^\sigma;\mathbf{r},\mathbf{r}'] = \arg\min_{\{\gamma^\sigma:\, \rho^\sigma(\mathbf{r})=\gamma^\sigma(\mathbf{r},\mathbf{r}),\, \gamma^\sigma=(\gamma^\sigma)^2\}} \int\int \delta(\mathbf{r}-\mathbf{r}')\left(-\frac{1}{2}\nabla_{\mathbf{r}}^2\gamma^\sigma(\mathbf{r},\mathbf{r}')\right) d^3\mathbf{r}d^3\mathbf{r}'. \tag{17.1b}$$

Among all idempotent 1-matrices with the correct electron density, the Levy constrained search selects the one with the lowest kinetic energy. This procedure is clearly impractical—it is actually more difficult to construct the Kohn–Sham kinetic energy associated with a specified density than it is to solve the Kohn–Sham equations [47–49]. We therefore proposed an explicit form for the 1-electron reduced matrix,

$$\tilde{\gamma}^\sigma[\rho^\sigma;\mathbf{r},\mathbf{r}'] = \sqrt{\rho^\sigma(\mathbf{r})\rho^\sigma(\mathbf{r}')}\,\tilde{g}\left(k_{\mathrm{F}}^\sigma[\rho^\sigma]\cdot|\mathbf{r}-\mathbf{r}'|\right), \tag{17.2}$$

where the function $\tilde{g}(x)$ must satisfy

$$\tilde{g}(0) = 1, \tag{17.3a}$$

$$\tilde{g}'(0) = 0, \tag{17.3b}$$

$$\tilde{g}''(0) < 1, \tag{17.3c}$$

$$-1 < \tilde{g}(x) \leq 1. \tag{17.3d}$$

In general, $\tilde{g}(x) < 0$ for some values of x [50]. Note that Eq. (17.2) is not an approximation: the exact functional is obtained by choosing Fermi wave vector as the 6-dimensional function,

$$k_{\mathrm{F}}^\sigma(\mathbf{r},\mathbf{r}') \equiv \frac{1}{|\mathbf{r}-\mathbf{r}'|}\tilde{g}^{-1}\left(\frac{\tilde{\gamma}^\sigma[\rho^\sigma;\mathbf{r},\mathbf{r}']}{\sqrt{\rho^\sigma(\mathbf{r})\rho^\sigma(\mathbf{r}')}}\right). \tag{17.4}$$

Equation (17.4) is also impractical, of course, so one needs to find practical approximations for the function $\tilde{g}(x)$.

17.2 Model One-Electron Reduced Density Matrices

In our previous work, we chose $\tilde{g}(x)$ based on its form in the uniform electron gas,

$$\tilde{g}_{\mathrm{LDA}}^{\sigma\sigma}(x) = 3\left(\frac{\sin x - x\cos x}{x^3}\right), \tag{17.5}$$

where $x = k_{\mathrm{F}}^{\sigma}(\mathbf{r},\mathbf{r}')|\mathbf{r}-\mathbf{r}'|$. This form, however, is not appropriate for molecules and other insulators, where the 1-electron reduced density matrix decays exponentially with increasing $|\mathbf{r}-\mathbf{r}'|$, with a rate of decay that tends to become faster as the band gap increases [51–56]. This suggests that one should add an exponential damping factor, which leads to a form like

$$\begin{aligned}\tilde{g}_{\exp}^{\sigma\sigma}\left(k_{\mathrm{F}}^{\sigma}(\mathbf{r},\mathbf{r}'),\ell_{\mathrm{F}}^{\sigma}(\mathbf{r},\mathbf{r}'),b\right) &= \tilde{g}_{\mathrm{LDA}}^{\sigma\sigma}\left(k_{\mathrm{F}}^{\sigma}(\mathbf{r},\mathbf{r}')|\mathbf{r}-\mathbf{r}'|\right)\\ &\times\exp\left[\frac{b(\mathbf{r},\mathbf{r}')}{\left|\ell_{\mathrm{F}}^{\sigma}(\mathbf{r},\mathbf{r}')\right|}\left(1-\sqrt{1+\left(\ell_{\mathrm{F}}^{\sigma}(\mathbf{r},\mathbf{r}')|\mathbf{r}-\mathbf{r}'|\right)^2}\right)\right].\end{aligned} \tag{17.6}$$

This form still has an infinite number of nodes, which is not realistic for molecular systems. Choosing an exponential model with a single node is perhaps more appropriate for molecular systems,

$$\begin{aligned}\tilde{g}_{\mathrm{IP}}^{\sigma\sigma}\left(k_{\mathrm{F}}^{\sigma}(\mathbf{r},\mathbf{r}'),a,b\right) &= \left(1-ak_{\mathrm{F}}^{\sigma}(\mathbf{r},\mathbf{r}')|\mathbf{r}-\mathbf{r}'|^2\right)\\ &\times\exp\left[\frac{b(\mathbf{r},\mathbf{r}')}{\left|\ell_{\mathrm{F}}^{\sigma}(\mathbf{r},\mathbf{r}')\right|}\left(1-\sqrt{1+\left(\ell_{\mathrm{F}}^{\sigma}(\mathbf{r},\mathbf{r}')|\mathbf{r}-\mathbf{r}'|\right)^2}\right)\right].\end{aligned} \tag{17.7}$$

It is reasonable to assume that the functional $b(\mathbf{r},\mathbf{r}')$ is related to the effective ionization potential (IP) at the location of interest, and so a reasonable form is [57–61]

$$b(\mathbf{r},\mathbf{r}') \propto \frac{1}{2}\left(\frac{1}{8}\frac{|\nabla\rho(\mathbf{r})|^2}{\rho^2(\mathbf{r})}+\frac{1}{8}\frac{|\nabla\rho(\mathbf{r}')|^2}{\rho^2(\mathbf{r}')}\right). \tag{17.8}$$

There is enormous flexibility in how one should select the nonlocal component of these functionals, but we choose a form inspired by the weighted density approximation,

$$k_{\mathrm{F}}^{\sigma}(\mathbf{r},\mathbf{r}') = \left[\frac{1}{2}\left(\left(k_{\mathrm{F}}^{\sigma}(\mathbf{r})\right)^p+\left(k_{\mathrm{F}}^{\sigma}(\mathbf{r}')\right)^p\right)\right]^{1/p}, \tag{17.9}$$

where p is a user-specified parameter. This form seems to work relatively well for the exchange and kinetic energies [10, 29, 30, 34–36, 41, 62, 63]. The form in Eq. (17.9) is motivated by the realization that in order to obtain the numerical benefits of orbital-free DFT, the quantities one is considering (here, $k_{\mathrm{F}}^{\sigma}(\mathbf{r},\mathbf{r}')$) must be approximated in terms of three-dimensional functions. Otherwise one could use the six-dimensional Kohn–Sham density matrix, $\gamma^{\sigma}(\mathbf{r}, \mathbf{r}')$, directly.

17.3 Constraints on Model One-Electron Reduced Density Matrices

The free parameters in model one-electron reduced density matrices should be chosen to satisfy exact constraints and, in particular, the Pauli principle. For example, the Kohn–Sham density matrix must be idempotent (cf. Eq. (17.1a)), which leads to the constraint

$$\tilde{\gamma}^{\sigma}(\mathbf{r}, \mathbf{r}'') = \int \tilde{\gamma}^{\sigma}(\mathbf{r}, \mathbf{r}')\tilde{\gamma}^{\sigma}(\mathbf{r}', \mathbf{r}'')d^3\mathbf{r}'. \tag{17.10}$$

As mentioned before, however, it is impractical to consider six-dimensional functions. The simplest way to express Eq. (17.10) as a three-dimensional constraint is to set $\mathbf{r} = \mathbf{r}''$. Then, using the form of the model density matrix (cf. Eq. (17.2)), we have

$$\rho^{\sigma}(\mathbf{r}) = \int \tilde{\gamma}^{\sigma}(\mathbf{r}, \mathbf{r}')\tilde{\gamma}^{\sigma}(\mathbf{r}', \mathbf{r})d^3\mathbf{r}' = \int \left(\sqrt{\rho^{\sigma}(\mathbf{r})}\tilde{g}^{\sigma}(\mathbf{r}, \mathbf{r}')\sqrt{\rho^{\sigma}(\mathbf{r}')}\right)^2 d^3\mathbf{r}', \tag{17.11}$$

which simplifies to the same constraint one uses in the weighted density approximation to the exchange hole [64–68],

$$1 = \int \rho^{\sigma}(\mathbf{r}') \left(\tilde{g}^{\sigma}(\mathbf{r}, \mathbf{r}')\right)^2 d^3\mathbf{r}'. \tag{17.12}$$

Using Eq. (17.12) gives reasonable results, but it is still far from the accuracy we need. This motivates the development of additional constraints.

For example, it is true that for any square-integrable function $\phi(\mathbf{r})$, it must be that

$$\int \tilde{\gamma}^{\sigma}(\mathbf{r}, \mathbf{r}'')\phi(\mathbf{r}'')d^3\mathbf{r}'' = \int\int \tilde{\gamma}^{\sigma}(\mathbf{r}, \mathbf{r}')\tilde{\gamma}^{\sigma}(\mathbf{r}', \mathbf{r}'')\phi(\mathbf{r}'')d^3\mathbf{r}'d^3\mathbf{r}''. \tag{17.13}$$

We clearly cannot force this constraint for all choices of $\phi(\mathbf{r}'')$ (this would be as difficult as enforcing the original idempotency constrain, Eq. (17.10)) but we can use specific functions that might be useful. For example, choosing $\phi(\mathbf{r}'')$ as an atomic $1s$ orbital will prevent the occupation number of that orbital from being too large. An especially simple form, however, is obtained when one uses $\phi(\mathbf{r}'') = \sqrt{\rho^{\sigma}(\mathbf{r}'')}$. Then one has:

$$\int \tilde{g}^{\sigma}(\mathbf{r}, \mathbf{r}'')\rho^{\sigma}(\mathbf{r}'')d^3\mathbf{r}'' = \int\int \tilde{g}^{\sigma}(\mathbf{r}, \mathbf{r}')\tilde{g}^{\sigma}(\mathbf{r}', \mathbf{r}'')\rho^{\sigma}(\mathbf{r}')\rho^{\sigma}(\mathbf{r}'')d^3\mathbf{r}'d^3\mathbf{r}''. \tag{17.14}$$

This constraint is more difficult to apply than Eq. (17.12) because it requires a six-dimensional numerical integration at each point $\mathbf{r}$. However, the same auxiliary basis-set methods that are used in efficient implementations of Eq. (17.12) could be used in Eq. (17.14) also [69]. If one considers $\phi(\mathbf{r})$ to be the gradient operator, then one obtains a constraint with the form of the March-Santamaria expression for the kinetic energy, namely [70–72]

$$\frac{1}{2}\int \left|\nabla_{\mathbf{r}}\tilde{\gamma}^{\sigma}(\mathbf{r},\mathbf{r}')\right|^2 d^3\mathbf{r}' = \frac{1}{2}\left[\nabla_{\mathbf{r}}\cdot\nabla_{\mathbf{r}'}\tilde{\gamma}^{\sigma}(\mathbf{r},\mathbf{r}')\right]_{\mathbf{r}=\mathbf{r}'}. \tag{17.15}$$

This constraint can be implemented with the same computational cost as Eq. (17.12), and helps ensure that the $\mathbf{r} \approx \mathbf{r}'$ portion of the model density matrix is accurate. The right-hand-side of Eq. (17.15) is just the (positive-definite) local kinetic energy [73, 74]. In fact, it is not difficult to see that Eq. (17.15) holds if the idempotency constraint holds near the diagonal,

$$\tilde{\gamma}^{\sigma}(\mathbf{r},\mathbf{r}+\varepsilon\hat{\mathbf{u}}) = \int \tilde{\gamma}^{\sigma}(\mathbf{r},\mathbf{r}')\tilde{\gamma}^{\sigma}(\mathbf{r}',\mathbf{r}+\varepsilon\hat{\mathbf{u}})d^3\mathbf{r}', \tag{17.16}$$

where $\hat{\mathbf{u}}$ is a unit vector. Equation (17.16) can be rewritten as

$$\tilde{g}^{\sigma}(\mathbf{r},\mathbf{r}+\varepsilon\hat{\mathbf{u}}) = \int \rho(\mathbf{r}')\tilde{g}^{\sigma}(\mathbf{r}',\mathbf{r}+\varepsilon\hat{\mathbf{u}})d^3\mathbf{r}'. \tag{17.17}$$

Expanding both sides in a Taylor series,

$$\begin{aligned}
\tilde{g}^{\sigma}(\mathbf{r},\mathbf{r}) &+ \varepsilon\left[\nabla_{\mathbf{r}''}\tilde{g}^{\sigma}(\mathbf{r},\mathbf{r}'')\right]_{\mathbf{r}''=\mathbf{r}}\cdot\hat{\mathbf{u}} + \varepsilon^2\hat{\mathbf{u}}^{\top}\left[\nabla_{\mathbf{r}''}\nabla_{\mathbf{r}''}^{\top}\tilde{g}^{\sigma}(\mathbf{r},\mathbf{r}'')\right]_{\mathbf{r}''=\mathbf{r}}\hat{\mathbf{u}} + \ldots \\
&= \int \rho(\mathbf{r}')\tilde{g}(\mathbf{r},\mathbf{r}')\left\{\tilde{g}^{\sigma}(\mathbf{r}',\mathbf{r}) + \varepsilon\left[\nabla_{\mathbf{r}''}\tilde{g}^{\sigma}(\mathbf{r}',\mathbf{r}'')\right]_{\mathbf{r}''=\mathbf{r}}\cdot\hat{\mathbf{u}}\right. \\
&\qquad \left. + \varepsilon^2\hat{\mathbf{u}}^{\top}\left[\nabla_{\mathbf{r}''}\nabla_{\mathbf{r}''}^{\top}\tilde{g}^{\sigma}(\mathbf{r}',\mathbf{r}'')\right]_{\mathbf{r}''=\mathbf{r}}\hat{\mathbf{u}} + \ldots\right\} d^3\mathbf{r}',
\end{aligned} \tag{17.18}$$

the right-hand-side of this equation simplifies due to Eq. (17.3),

$$\begin{aligned}
\tilde{g}^{\sigma}(\mathbf{r},\mathbf{r}) &+ \varepsilon\left[\nabla_{\mathbf{r}''}\tilde{g}^{\sigma}(\mathbf{r},\mathbf{r}'')\right]_{\mathbf{r}''=\mathbf{r}}\cdot\hat{\mathbf{u}} + \varepsilon^2\hat{\mathbf{u}}^{\top}\left[\nabla_{\mathbf{r}''}\nabla_{\mathbf{r}''}^{\top}\tilde{g}^{\sigma}(\mathbf{r},\mathbf{r}'')\right]_{\mathbf{r}''=\mathbf{r}}\hat{\mathbf{u}} + \ldots \\
&= 1 + \varepsilon^2\hat{\mathbf{u}}^{\top}\left[\nabla_{\mathbf{r}''}\nabla_{\mathbf{r}''}^{\top}\tilde{g}^{\sigma}(\mathbf{r},\mathbf{r}'')\right]_{\mathbf{r}''=\mathbf{r}}\hat{\mathbf{u}} + \ldots.
\end{aligned} \tag{17.19}$$

Then, equating terms in the expansions order-by-order, one has an infinite set of constraints, of which the lowest-order ones are most important and easiest to apply,

$$1 = \int \rho(\mathbf{r}')\left(\tilde{g}^{\sigma}(\mathbf{r},\mathbf{r}')\right)^2 d^3\mathbf{r}', \tag{17.20a}$$

$$0 = \int \rho(\mathbf{r}')\tilde{g}^{\sigma}(\mathbf{r},\mathbf{r}')\nabla_{\mathbf{r}}\tilde{g}^{\sigma}(\mathbf{r}',\mathbf{r})d^3\mathbf{r}'$$

$$= \int \rho(\mathbf{r}')\nabla_{\mathbf{r}} \left(\tilde{g}^{\sigma}(\mathbf{r},\mathbf{r}')\right)^2 d^3\mathbf{r}', \tag{17.20b}$$

$$\left[\nabla_{\mathbf{r}''}\nabla_{\mathbf{r}''}^{\top}\tilde{g}^{\sigma}(\mathbf{r},\mathbf{r}'')\right]_{\mathbf{r}''=\mathbf{r}} = \int \rho(\mathbf{r}')\tilde{g}^{\sigma}(\mathbf{r},\mathbf{r}')\nabla_{\mathbf{r}}\nabla_{\mathbf{r}}^{\top}\tilde{g}^{\sigma}(\mathbf{r}',\mathbf{r})d^3\mathbf{r}', \tag{17.20c}$$

$$\vdots$$

The first of these equations is just the original diagonal condition, Eq. (17.12), which is equivalent to the weighted density approximation equation for the normalization of the exchange hole,

$$-1 = \int \rho(\mathbf{r}')h_x(\mathbf{r},\mathbf{r}')d^3\mathbf{r}'. \tag{17.21}$$

The second equation also can be seen as a constraint on the model density matrix but also on the exchange hole for weighted density approximations,

$$0 = \int \rho(\mathbf{r}')\nabla_{\mathbf{r}}h_x(\mathbf{r},\mathbf{r}')d^3\mathbf{r}'. \tag{17.22}$$

It is just the gradient of both sides of Eq. (17.21), so it should hold automatically when Eq. (17.21) is true. The third constraint in Eq. (17.20) is nontrivial, and cannot be easily written as a constraint on the exchange hole. Overall, Eq. (17.20) are a hierarchy of constraints and, if the full hierarchy is imposed, then the model one-electron reduced density matrix, and the kinetic energy density functional it implies, is guaranteed to be N-representable. Philosophically, then, Eq. (17.20) are similar to other methods for developing density functionals based on hierarchies of constraints [72, 75–83].

17.4 Summary

Approximating the kinetic energy as an explicit functional of the electron density has proven to be a very difficult task, we propose to explore a strategy based on modelling the one-electron density matrix using a weighted density approximation. We propose that the parameters in the weighted density approximation should be determined by constraints associated with its idempotency, and propose Eqs. (17.14) and (17.15) as additions to the usual weighted density approximation condition, Eq. (17.12). In particular, the March-Santamaria identity inspires the hierarchy of derivative constraints in Eq. (17.20); these seem especially promising since they are directly linked to the requirement that the accuracy of the kinetic energy from the model density matrix and, specifically, require that different ways of calculating the kinetic energy from the model density matrix give the same results. In order to simultaneously satisfy constraints Eq. (17.20), one needs a more flexible form for the model density matrix than is provided when one uses the uniform electron gas.

The damped local density approximation model given in Eq. (17.7) is merely one possibility.

The weighted density approximation for the one-electron reduced density matrix, Eq. (17.2), is a very flexible form, and there are an infinite number of potentially useful constraints that can be imposed upon it. We expect that further investigations along these lines will provide more accurate kinetic energy functionals, though innovations are also required so that constraints like Eq. (17.20) can be efficiently imposed. We will address these numerical problems in a follow-up paper [84].

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