

Correlated and idempotent Dirac first-order density matrices with identical diagonal Fermion density: a route to extract a one-body potential energy in TDDFT

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Abstract After a brief introduction to the use of the idempotent Dirac first-order density matrix (DM), its time-dependent generalization is considered. Special attention is focused on the equation of motion for the time-dependent DM, which is characterized by the one-body potential $V(\mathbf{r}, t)$ of time-dependent density functional theory. It is then shown how the force $-\nabla V(\mathbf{r}, t)$ can be extracted explicitly from this equation of motion. Following a linear-response treatment in which a weak potential $V(\mathbf{r}, t)$ is switched on to an initially uniform electron gas, the non-linear example of the two-electron spin-compensated Moshinsky atom is a further focal point. We demonstrate explicitly how the correlated DM for this model can be constructed from the idempotent Dirac DM, in this time-dependent example.

Keywords Time-dependent density functional theory · Linear response theory · Moshinsky atom

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1 Background and outline

The origins of the present article concerned with idempotent first-order density matrices (DM) can be traced back, at very least, to the work of Dirac [1] in the early years of Schrödinger wave mechanics. Dirac's aim was to introduce exchange into the Thomas-Fermi statistical method (see for example [2]), forerunner of modern density functional theory [3]. In this same context, a further major advance was made by Slater [4] (see also [5]), who was concerned with a simplification of the Hartree-Fock approximation. In particular, Slater proposed to replace the Fock operator by a suitably chosen one-body potential energy $V(\mathbf{r})$. Slater's work on this quantity $V(\mathbf{r})$ was formally completed by Kohn and Sham [6]. Already, in his 1951 paper, to approximate $V_x(\mathbf{r})$, Slater appealed to Dirac's single-particle (s) idempotent density matrix [1] which is based on a single Slater determinant built from occupied orbitals $\phi_i(\mathbf{r})$:

$$\gamma_s(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^N \phi_i^*(\mathbf{r})\phi_i(\mathbf{r}'), \quad (1)$$

i is running from 1 to N in a system with N electrons, with diagonal density

$$n(\mathbf{r}) = \gamma_s(\mathbf{r}, \mathbf{r}')|_{\mathbf{r}'=\mathbf{r}} = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2. \quad (2)$$

Slater invoked Dirac's total exchange energy, denoted E_x below, calculated from such a Slater determinant as (here and in the following we use atomic units)

$$E_x = -\frac{1}{4} \iint \frac{\gamma_s^2(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}'. \quad (3)$$

Defining, though not uniquely, an exchange energy density

$$\epsilon_x(\mathbf{r}) = -\frac{1}{4} \int \frac{\gamma_s^2(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \quad (4)$$

Slater proposed a definition of an approximate one-body exchange potential, denoted below by $V_x^{\text{Sl}}(\mathbf{r})$ as

$$V_x^{\text{Sl}}(\mathbf{r}) = \frac{2\epsilon_x(\mathbf{r})}{n(\mathbf{r})}, \quad (5)$$

with $n(\mathbf{r})$ the ground-state electron density. Subsequent work by one of us [7] proved that in atoms, molecules and clusters sufficiently far from all nuclei

$$\epsilon_x(\mathbf{r}) \rightarrow -\frac{1}{2r}n(r), \quad (6)$$

and hence from Eq. 5, $V_x^{SI}(\mathbf{r}) \rightarrow -1/r$ as required for the correct self-interaction correction.

Stimulated by the work of Kohn and Sham [6], it is now generally assumed that the exact ground-state electron density $n(\mathbf{r})$ of molecules and clusters can be reproduced by a choice of one-body potential $V(\mathbf{r})$ of the form

$$V(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}), \quad (7)$$

with the external potential $V_{\text{ext}}(\mathbf{r})$ and Hartree potential $V_H(\mathbf{r})$. Unfortunately, the exchange-correlation potential $V_{xc}(\mathbf{r})$ in Eq. 7 is presently not known, and its exact form constitutes a truly major theoretical problem.

However, given a potential $V(\mathbf{r})$, the early study of March and Murray [8,9] gave a perturbation theory to all orders in $V(\mathbf{r})$ for the Dirac density matrix $\gamma_s(\mathbf{r}, \mathbf{r}')$ introduced above, the unperturbed system being the homogeneous electron gas. Their result has the form

$$\gamma_s(\mathbf{r}, \mathbf{r}', E) - \gamma_s^0(\mathbf{r}, \mathbf{r}', E) = \sum_{i=1}^{\infty} \gamma_s^i(\mathbf{r}, \mathbf{r}', E), \quad (8)$$

where γ_s^i is $o(V^i)$ and is given quite explicitly by March and Murray [9]. On the diagonal $\mathbf{r}' = \mathbf{r}$, they showed that the series in Eq. 8 could be summed to all orders in $V(\mathbf{r})$, yielding the Thomas-Fermi ground-state electron density $n_{\text{TF}}(\mathbf{r})$ as

$$n_{\text{TF}}(\mathbf{r}) = \frac{8^{\frac{1}{2}}}{3\pi^2} [\mu - V(\mathbf{r})]^{\frac{3}{2}}, \quad (9)$$

provided $V(\mathbf{r})$ varies by but a fraction of itself over a spatial distance of order of the de Broglie wavelength for an electron at the Fermi energy, equal to the chemical potential μ entering Eq. 9. Thus, on the diagonal, Eq. 8 can be described as an exact Thomas-Fermi method in perturbation theory [10].

Suppose now, in a true non-relativistic description of a N -electron molecule, the normalized Schrödinger ground-state wave function (suppressing spin for notational convenience) is $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$. The exact first-order density matrix (DM) $\gamma(\mathbf{r}, \mathbf{r}')$ is defined (see for example [11]) as

$$\gamma(\mathbf{r}, \mathbf{r}') = N \int \Psi^*(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi(\mathbf{r}', \mathbf{r}_2, \dots, \mathbf{r}_N) d\mathbf{r}_2, \dots, d\mathbf{r}_N, \quad (10)$$

where obviously $\gamma(\mathbf{r}, \mathbf{r}')|_{\mathbf{r}'=\mathbf{r}} = n(\mathbf{r})$, the exact ground-state density of the N -electron molecule under consideration.

Since the calculation of Ψ for more than a few electrons continues to be a formidable computational task, current trends are to focus on the Dirac idempotent matrix $\gamma_s(\mathbf{r}, \mathbf{r}')$, rather than the correlated DM $\gamma(\mathbf{r}, \mathbf{r}')$, but with both these matrices having, in principle, identical (and hopefully eventually exact!) ground-state density $n(\mathbf{r})$.

Therefore, the central problem in density functional theory (DFT) [3] is the construction of the one-body potential $V(\mathbf{r})$ in Eq. 7. Then knowing $n(\mathbf{r})$ the Hartree

potential may be calculated, and all important is the remaining exchange-correlation contribution $V_{xc}(\mathbf{r})$. Presently this quantity remains unknown, though many approximations exist for it. Perturbative procedures that are guaranteed to converge on the exact form of $V_{xc}(\mathbf{r})$ are also available [12–14]. In practice, however, going beyond the exchange-only approximation involves already a high degree of numerical complexity.

The accuracy of a given approximation for V_{xc} can always be assessed *a posteriori*, by comparison of some derived properties, like lattice constants or excitation energies, against experiment. In order to improve on existing approximations, it would be highly desirable to compare these approximations against exact or near-exact forms of V_{xc} directly. Given that highly accurate calculations on correlated few-electron systems are available nowadays, the question arises how this information may be used to extract the one-body potential $V(\mathbf{r})$ of DFT or $V(\mathbf{r}, t)$ of time-dependent DFT (TDDFT) [15]. For the ground state theory, a numerical method to perform this task for arbitrary many-electron systems has been proposed by Zhao, Morrison and Parr [16–18]. If one confines oneself to the special case of spin-compensated two-electron systems the procedure is (apart from numerical difficulties) even simpler: The exact electron density is easily related to the single Kohn–Sham orbital of the system and inversion of the Kohn–Sham equation yields the desired exchange correlation potential. This inversion is possible both for stationary [19] as well as time-dependent [20, 21] problems. Although the mapping between densities and potentials is formally guaranteed even for TDDFT [22], a practical realization of this relation beyond two-electron system remains elusive.

Therefore, in the following Sects. 2 and 3 we shall report on how the one-body potential $V(\mathbf{r}, t)$ might, at least in principle, become accessible via first-order Dirac density matrices, without the need to resort to the determination of individual Kohn–Sham states. An important question is then how these density matrices may be obtained from correlated many-particle calculations. Section 4 explicitly addresses this issue for the Moshinsky model and illustrates the relation between the correlated and Dirac DM, which turns out to be surprisingly simple in the examined case. In all of these investigations, we cover both the stationary and the more general time-dependent case. A brief summary finally constitutes Sect. 5.

2 Force expressions and equation of motion for the Dirac density matrix

2.1 Stationary case

In early work on the Dirac density matrix, March and Young [23] obtained expressions, in one dimension, for the force $-\nabla V(\mathbf{r})$ in terms of γ_s , by expansion around the diagonal. The three-dimensional generalization of their result reads

$$\left[\nabla_{\mathbf{r}}^2 - \nabla_{\mathbf{r}'}^2 \right] \gamma_s(\mathbf{r}, \mathbf{r}') = 2 [V(\mathbf{r}) - V(\mathbf{r}')] \gamma_s(\mathbf{r}, \mathbf{r}'), \quad (11)$$

which is readily verified by substituting Eq. 1 into the above equation, and then invoking the Schrödinger equation for the orbitals $\phi_i(\mathbf{r})$ generated by the one-body potential

$V(\mathbf{r})$. Dividing both sides of Eq. 11 by γ_s and then applying the gradient operator yields the force as

$$-\nabla V(\mathbf{r}) = -\frac{1}{2}\nabla_{\mathbf{r}} \left[\frac{(\nabla_{\mathbf{r}}^2 - \nabla_{\mathbf{r}'}^2)\gamma_s(\mathbf{r}, \mathbf{r}')}{\gamma_s(\mathbf{r}, \mathbf{r}')} \right]. \tag{12}$$

2.2 Time-dependent case

Given one-electron wave functions $\phi_i(\mathbf{r}, t)$ generated via the Schrödinger equation

$$\left[-\frac{1}{2}\nabla^2 + V(\mathbf{r}, t) \right] \phi_i(\mathbf{r}, t) = i \frac{\partial \phi_i(\mathbf{r}, t)}{\partial t}, \tag{13}$$

from a chosen time-dependent potential $V(\mathbf{r}, t)$, the natural generalization of the Dirac single-particle static density matrix is to write

$$\gamma_s(\mathbf{r}, \mathbf{r}', t) = \sum_{i=1}^N \phi_i^*(\mathbf{r}, t)\phi_i(\mathbf{r}', t). \tag{14}$$

Then the generalization of the static equation of motion given in Eq. 11 is readily found to be

$$[V(\mathbf{r}, t) - V(\mathbf{r}', t)]\gamma_s(\mathbf{r}, \mathbf{r}', t) = \left[-i\frac{\partial}{\partial t} + \frac{1}{2}(\nabla_{\mathbf{r}}^2 - \nabla_{\mathbf{r}'}^2) \right] \gamma_s(\mathbf{r}, \mathbf{r}', t) \tag{15}$$

Dividing both sides in Eq. 15 by γ_s , one then can take the gradient of the resulting equation to find the equation of motion for γ_s :

$$-\nabla V(\mathbf{r}, t) = i\nabla_{\mathbf{r}} \frac{\partial}{\partial t} \ln \gamma_s(\mathbf{r}, \mathbf{r}', t) - \frac{1}{2}\nabla_{\mathbf{r}} \left[\frac{(\nabla_{\mathbf{r}}^2 - \nabla_{\mathbf{r}'}^2)\gamma_s(\mathbf{r}, \mathbf{r}', t)}{\gamma_s(\mathbf{r}, \mathbf{r}', t)} \right], \tag{16}$$

which is the desired generalization of the static force Eq. 12. The potential $V(\mathbf{r}, t)$ and hence also $V_{xc}(\mathbf{r}, t)$ is now accessible by a path independent line integral similar to the proceeding in [24]. We note that the resulting potential will in general depend on the chosen initial state of the system under study [25–27].

3 Response function of the homogeneous electron gas (HEG)

3.1 Stationary case

The \mathbf{r} space form of the linear response function of the HEG was obtained in the study of March and Murray [8]. Writing the density change $\Delta n(\mathbf{r}) = n(\mathbf{r}) - n_0$ due to switching on a potential $V(\mathbf{r})$ to the HEG as

$$\Delta n(\mathbf{r}) = \int F_0(|\mathbf{r} - \mathbf{r}'|) V(\mathbf{r}') d\mathbf{r}', \quad (17)$$

the result of [8] was

$$F_0(|\mathbf{r} - \mathbf{r}'|) = -\frac{k_f^2}{2\pi^3} \frac{j_1(k_f |\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|^2}. \quad (18)$$

Here, $j_1(x)$ is the first-order spherical Bessel function $(\sin x - x \cos x)/x^2$, k_f being the Fermi momentum of the HEG. The time-dependent generalization of their result will be considered in Sect. 3.2 below. For a periodic (p) lattice, Stoddart, March and Stott [28] have obtained an expression for the energy derivative of the response function F : namely $\partial F/\partial E$. Their result requires the lattice Green function $G_p(\mathbf{r}, \mathbf{r}', E)$ as well as the Dirac density matrix γ_p , and takes the explicit form

$$\frac{\partial F_p}{\partial E} = 2\Re \left\{ G_p(\mathbf{r}, \mathbf{r}', E) \frac{\partial \gamma_p(\mathbf{r}, \mathbf{r}', E)}{\partial E} \right\}. \quad (19)$$

Inserting free-electron forms for the Green function and the density matrix into Eq. 19 readily yields back Eq. 18 with $k_f^2/2 = E$.

3.2 Time-dependent case

In this section we consider the scattering of free-electrons from a local and time-dependent potential $V(\mathbf{r}, t)$ that is adiabatically turned on in the remote past. We additionally assume that the potential is weak enough to apply linear response theory. In Dirac notation the scattering states fulfill the time-dependent Schrödinger equation in the following form

$$\left(i \frac{\partial}{\partial t} - \hat{H}_0 \right) |\psi_i, t\rangle = \hat{V}(t) |\psi_i, t\rangle; \quad \hat{H}_0 = \frac{p^2}{2}. \quad (20)$$

Introducing the unperturbed free-particle states $|\phi_i, t\rangle$, Eq. 20 may be equally well written in integral form as the Lippmann–Schwinger equation (see e.g. [29])

$$|\psi_i, t\rangle = |\phi_i, t\rangle + \int_{-\infty}^{\infty} \hat{G}(t, t') \hat{V}(t') |\psi_i, t'\rangle dt', \quad (21)$$

where the retarded Green function $\hat{G}(t, t')$ is defined generally by

$$\left(i \frac{\partial}{\partial t} - \hat{H} \right) \hat{G}(t, t') = \delta(t - t'), \quad (22)$$

with the boundary condition $\hat{G}(t, t') = 0$ for $t < t'$. The solution to Eq. 22 for arbitrary \hat{H} is known and takes the following form in the position representation

$$G(\mathbf{r}, t, \mathbf{r}', t') = \langle \mathbf{r} | \hat{G}(t, t') | \mathbf{r}' \rangle = -i\Theta(t - t') \langle \mathbf{r} | e^{-i\hat{H}(t-t')} | \mathbf{r}' \rangle, \tag{23}$$

$\Theta(t - t')$ being the Heaviside step function. The Green function $G(\mathbf{r}, t, \mathbf{r}', t')$ is equivalent to the propagator in Feynman’s path integral formulation of quantum mechanics and can be easily evaluated for the free particle case at hand, where $\hat{H} = \hat{H}_0$. The result in three spatial dimensions reads [30]

$$G_0(\mathbf{r}, t, \mathbf{r}', t') = -i\Theta(t - t') [2\pi i(t - t')]^{-\frac{3}{2}} \exp \left[\frac{i|\mathbf{r} - \mathbf{r}'|^2}{2(t - t')} \right]. \tag{24}$$

In order to arrive at an expression for the time-dependent density $n(\mathbf{r}, t)$, we write the Lippmann–Schwinger Eq. 21 in the position representation

$$\psi_i(\mathbf{r}, t) = \phi_i(\mathbf{r}, t) + \int \int_{-\infty}^{\infty} G_0(\mathbf{r}, t, \mathbf{r}', t') V(\mathbf{r}', t') \psi_i(\mathbf{r}', t') d\mathbf{r}' dt', \tag{25}$$

where we have used the locality of the potential. Here, the free particle states $\phi_i(\mathbf{r}, t)$ with wave vector \mathbf{k}_i are normalized to the volume Ω

$$\phi_i(\mathbf{r}, t) = \frac{1}{\sqrt{\Omega}} \exp \left[i \left(\mathbf{k}_i \mathbf{r} - \frac{1}{2} k_i^2 t \right) \right]. \tag{26}$$

Multiplying this equation by $\psi_i^*(\mathbf{r}, t)$ from the left and summing over all occupied states i , the induced density change is obtained. Using Eq. 25 and working to linear order in $V(\mathbf{r}, t)$, which is equivalent to the first-order Born approximation, we find

$$n(\mathbf{r}, t) - n_0 = 2\Re \left\{ \int \int_{-\infty}^{\infty} G_0(\mathbf{r}, t, \mathbf{r}', t') \tilde{\gamma}_0(\mathbf{r}, t, \mathbf{r}', t') \right\} V(\mathbf{r}', t') d\mathbf{r}' dt', \tag{27}$$

with $n_0 = N/V$ and the generalized zero-order density matrix $\tilde{\gamma}_0$ cf. Eq. 14

$$\tilde{\gamma}_0(\mathbf{r}, t, \mathbf{r}', t') = \sum_{i=1}^N \phi_i^*(\mathbf{r}, t) \phi_i(\mathbf{r}', t'), \tag{28}$$

which implicitly depends on the energy ($E = k_f^2/2$) of the highest occupied orbital with wave vector k_f .

We are now in the position to define the time-dependent response function $F_0(\mathbf{r}, t, \mathbf{r}', t')$ according to

$$\begin{aligned}\Delta n(\mathbf{r}, t) &= n(\mathbf{r}, t) - n_0 \\ &= \int_{-\infty}^{\infty} \int F_0(\mathbf{r}, t, \mathbf{r}', t') V(\mathbf{r}', t') d\mathbf{r} dt',\end{aligned}\quad (29)$$

and observe that due to Eq. 24 its energy derivative may be written as

$$\frac{\partial F_0}{\partial E} = 2\Re \left\{ G_0(\mathbf{r}, t, \mathbf{r}', t') \frac{\partial \tilde{\gamma}_0(\mathbf{r}, t, \mathbf{r}', t')}{\partial E} \right\}, \quad (30)$$

which is precisely the form that was also found in the time-independent Eq. 19 of Sect. 3. Further progress is made by evaluating the time-dependent Dirac density matrix $\tilde{\gamma}_0(\mathbf{r}, t, \mathbf{r}', t')$ of the unperturbed system. For Ω tending to infinity, the summation in Eq. 28 may be replaced by an integration over energy which yields the following somewhat complicated result

$$\begin{aligned}\tilde{\gamma}_0(\mathbf{r}, t, \mathbf{r}', t') &= -4i \left\{ \frac{k_f}{\pi^2(t-t')} j_0(k_f |\mathbf{r} - \mathbf{r}'|) \exp \left[\frac{i}{2}(t-t')k_f^2 \right] \right. \\ &\quad - [2\pi i(t-t')]^{-\frac{3}{2}} \exp \left[-\frac{i|\mathbf{r} - \mathbf{r}'|^2}{2(t-t')} \right] \\ &\quad \times \left[\operatorname{erf} \left(\sqrt{\frac{-i|\mathbf{r} - \mathbf{r}'|^2}{2(t-t')}} \left(1 + k_f \frac{(t-t')}{|\mathbf{r} - \mathbf{r}'|} \right) \right) \right. \\ &\quad \left. \left. - \operatorname{erf} \left(\sqrt{\frac{-i|\mathbf{r} - \mathbf{r}'|^2}{2(t-t')}} \left(1 - k_f \frac{(t-t')}{|\mathbf{r} - \mathbf{r}'|} \right) \right) \right] \right\}\end{aligned}\quad (31)$$

with $j_0(x) = \sin(x)/x$ and where we define the error function as

$$\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-t^2) dt. \quad (32)$$

This result can be shown, after some manipulations, to be equivalent to the earlier solution of March and Tosi ([31], Eq. A9 of that publication) of the same problem, who use a slightly different form of representation.

We now consider two limiting cases: For dilute electron gases—that is small k_f —the term $k_f(t-t')/|\mathbf{r} - \mathbf{r}'|$ tends to zero for detection far away from the scatterer and fixed detection time. In this case the difference of the two error functions in Eq. 31 tends to zero. In the opposite limit of high densities, as in metals with typical Fermi

velocities on the order of 10^6 m/s, the difference of the error functions is purely real, since for real a , $\lim_{a \rightarrow \infty} \operatorname{erf}(\sqrt{i}a) = \operatorname{sgn}(a)$. In both cases, therefore, combination of Eqs. 24, 27, and 31 leads to the following simplified result for the time-dependent generalization of the HEG response function (cf. Eq. 18)

$$F_0(\mathbf{r}, t, \mathbf{r}', t') \approx \sqrt{\frac{8}{\pi(t-t')^5}} k_f j_0(k_f |\mathbf{r} - \mathbf{r}'|) \cos \left[\frac{|\mathbf{r} - \mathbf{r}'|^2}{2(t-t')} - \frac{(t-t')}{2} k_f^2 + \frac{\pi}{4} \right], \tag{33}$$

while the exact solution can be easily evaluated along the same lines.

Taking advantage of the fact that the response function Eq. 33 is homogeneous both in space and time we now consider the Fourier transform of the induced electron density $\Delta n(\mathbf{r}, t)$

$$\Delta n(\mathbf{q}, \omega) = \iint \Delta n(\mathbf{r}, t) e^{i\mathbf{q}\mathbf{r}} e^{-i\omega t} d\mathbf{r} dt, \tag{34}$$

which allows us to extract the one-body potential from Eq. 29 by use of the convolution theorem

$$V(\mathbf{q}, \omega) = \frac{\Delta n(\mathbf{q}, \omega)}{F_0(\mathbf{q}, \omega)}, \tag{35}$$

provided the density response is known. Solution of Eq. 35 requires the knowledge of $F_0(\mathbf{q}, \omega)$ and it turns out that the analytical evaluation of the Fourier transform of Eq. 33 (or even the exact result) is very demanding. Fortunately, $F_0(\mathbf{q}, \omega)$ has been explicitly given by Lindhard already in the 1950s using a reciprocal space approach [32,33]. This reduces the complexity of a numerical treatment of Eq. 35 that will in general be necessary.

4 Correlated and idempotent density matrix of the Moshinsky atom

4.1 Stationary case

In this section, we illustrate the relation between correlated and idempotent density matrices by the simple example of a spin-compensated two-electron atom with harmonic confinement. This analytically solvable model was put forward by Moshinsky [34] in the 1960s and is characterized by the following Hamiltonian:

$$\hat{H} = -\frac{1}{2} (\nabla_{r_1}^2 + \nabla_{r_2}^2) + \frac{1}{2} \omega_0^2 (r_1^2 + r_2^2) + \frac{1}{2} K(\mathbf{r}_1 - \mathbf{r}_2)^2. \tag{36}$$

The electron density for this system is found to be of Gaussian form (see for example [35])

$$n(\mathbf{r}) = 2 \left(\frac{\mu\omega_0}{\pi} \right)^{3/2} \exp(-\mu\omega_0 r^2), \quad \mu = 2 \left[1 + \left(1 + \frac{2K}{\omega_0^2} \right)^{-1/2} \right]^{-1}, \quad (37)$$

with the dimensionless parameter μ that tends to one as the interaction strength K tends to zero. March [36] recently evaluated the model's correlated first-order density matrix and was able to express it entirely in terms of the electron density, thereby explicitly confirming the first Hohenberg–Kohn theorem for this particular example. His result reads

$$\gamma(\mathbf{r}_1, \mathbf{r}_2) = c_\gamma \left[n \left(\sqrt{r_1^2 + r_2^2} \right) \right]^{v/\mu} [n(|\mathbf{r}_1 + \mathbf{r}_2|)]^{\eta/\mu} \quad \text{with} \quad (38)$$

$$c_\gamma = \left[2 \left(\frac{\mu\omega_0}{\pi} \right)^{3/2} \right]^{\frac{\mu-v-\eta}{\mu}}, \quad v = \frac{1}{2(2-\mu)}, \quad \eta = \frac{1}{4}(\mu - 2v), \quad (39)$$

where the constant c_γ is also related to the density (at $\mathbf{r} = 0$).

Now we would like to go one step further and relate the DM to the Dirac density matrix γ_s with equal diagonal. In this spin-compensated two-electron example, there is only one occupied single-particle orbital ϕ , which is therefore easily related to the density ($\phi(\mathbf{r}) = \sqrt{n(\mathbf{r})/2}$).

Taking advantage of this fact, we note that γ_s may be written as

$$\begin{aligned} \gamma_s(\mathbf{r}_1, \mathbf{r}_2) &= n(\mathbf{r}_1)^{\frac{1}{2}} n(\mathbf{r}_2)^{\frac{1}{2}} \\ &= 2 \left(\frac{\mu\omega_0}{\pi} \right)^{3/2} \exp \left[-\frac{\mu\omega_0}{2} (r_1^2 + r_2^2) \right]. \end{aligned} \quad (40)$$

Comparing Eqs. 37, 38, and 40 we see that both γ and γ_s exhibit quadratic forms in the exponentials so that we may set

$$\gamma(\mathbf{r}_1, \mathbf{r}_2) = \gamma_s(\mathbf{r}'_1, \mathbf{r}'_2), \quad (41)$$

with yet to be determined $\mathbf{r}'_1, \mathbf{r}'_2$, that are linear in $\mathbf{r}_1, \mathbf{r}_2$. This surprisingly simple result holds for all values of the interaction strength.

In principle, there is an infinite number of solutions for Eq. 41. We enforce a special one by choosing the Ansatz:

$$\begin{aligned} \mathbf{r}'_1 &= a \mathbf{r}_1 + b \mathbf{r}_2 \\ \mathbf{r}'_2 &= b \mathbf{r}_1 + a \mathbf{r}_2, \end{aligned} \quad (42)$$

with unknown constants a and b . Inserting Eq. 42 into Eq. 41, a comparison of coefficients leads to

$$\mu ab = \eta \tag{43}$$

$$\mu(a - b)^2 = 2v, \tag{44}$$

with one particular solution given by

$$a = \left[\frac{v + \eta + \sqrt{v^2 + 2v\eta}}{\mu} \right]^{\frac{1}{2}} \tag{45}$$

$$b = \frac{\eta}{\mu} \left[\frac{v + \eta + \sqrt{v^2 + 2v\eta}}{\mu} \right]^{-\frac{1}{2}}.$$

In the limit of vanishing interaction

$$\lim_{K \rightarrow 0} a = 1; \quad \lim_{K \rightarrow 0} b = 0; \quad \Rightarrow \quad \lim_{K \rightarrow 0} \gamma(\mathbf{r}_1, \mathbf{r}_2) = \gamma_s(\mathbf{r}_1, \mathbf{r}_2), \tag{46}$$

the correlated first-order density matrix equals the Dirac density matrix, as expected.

4.2 Time-dependent case

We now turn to generalizations of the results in Sect. 4.1. The time-dependent Moshinsky model has already been studied earlier by the present authors [37] in the wider scope of harmonically confined two-electron systems with general inter-particle interaction $u(r)$. The relevant Hamiltonian for this problem is given by

$$\hat{H} = -\frac{1}{2} (\nabla_{r_1}^2 + \nabla_{r_2}^2) + \frac{1}{2} \omega_0^2(t) (r_1^2 + r_2^2) + u(|\mathbf{r}_1 - \mathbf{r}_2|). \tag{47}$$

Separation into center-of-mass (cm) and relative-motion (rm) channels with respective coordinates $\mathbf{c} = 1/2(\mathbf{r}_1 + \mathbf{r}_2)$ and $\mathbf{b} = (\mathbf{r}_1 - \mathbf{r}_2)$, leads to the following equations of motion

$$i \frac{\partial}{\partial t} \psi_{\text{cm}}(\mathbf{c}, t) = \left[-\frac{1}{2m_{\text{cm}}} \nabla_{\mathbf{c}}^2 + \frac{m_{\text{cm}}}{2} \omega_0^2(t) c^2 \right] \psi_{\text{cm}}(\mathbf{c}, t) \tag{48}$$

$$i \frac{\partial}{\partial t} \psi_{\text{rm}}(\mathbf{b}, t) = \left[-\frac{1}{2m_{\text{rm}}} \nabla_{\mathbf{b}}^2 + \frac{m_{\text{rm}}}{2} \omega_0^2(t) b^2 + u(b) \right] \psi_{\text{rm}}(\mathbf{b}, t), \tag{49}$$

with effective masses $m_{\text{cm}} = 2$ and $m_{\text{rm}} = 1/2$. The cm Schrödinger equation can be solved analytically in three dimensions. For the special but non-trivial case of a system initially in its ground-state at $t = 0$ we find the result (see also [20])

$$\psi_{\text{cm}}(\mathbf{c}, t) = \left(\frac{m_{\text{cm}} \dot{\phi}_{\text{cm}}(t)}{\pi} \right)^{3/4} \exp \left[-\frac{1}{2} m_{\text{cm}} \left(\dot{\phi}_{\text{cm}}(t) - i \frac{d \ln |X_{\text{cm}}(t)|}{dt} \right) c^2 \right], \quad (50)$$

where the functions $\phi_{\text{cm}}(t)$ and $X_{\text{cm}}(t)$ are determined by the solution of the *classical* equation of motion

$$\begin{aligned} \ddot{X}_{\text{cm}}(t) &= -\omega_0^2(t) X_{\text{cm}}(t) \\ X_{\text{cm}}(t) &= |X_{\text{cm}}(t)| e^{i\phi_{\text{cm}}(t)}. \end{aligned} \quad (51)$$

The rm Schrödinger equation is in general difficult to solve for typical inter-particle potentials, the Moshinsky model characterized by $u(b) = \frac{1}{2} K b^2$ being an exception. Here, the rm problem is seen to be isomorphic to the cm one and its solution is given by

$$\psi_{\text{rm}}(\mathbf{b}, t) = \left(\frac{m_{\text{rm}} \dot{\phi}_{\text{rm}}(t)}{\pi} \right)^{3/4} \exp \left[-\frac{1}{2} m_{\text{rm}} \left(\dot{\phi}_{\text{rm}}(t) - i \frac{d \ln |X_{\text{rm}}(t)|}{dt} \right) b^2 \right], \quad (52)$$

with

$$\begin{aligned} \ddot{X}_{\text{rm}}(t) &= -\left(\omega_0^2(t) + \frac{K}{m_{\text{rm}}} \right) X_{\text{rm}}(t) \\ X_{\text{rm}}(t) &= |X_{\text{rm}}(t)| e^{i\phi_{\text{rm}}(t)}. \end{aligned} \quad (53)$$

As a further result, we now continue to evaluate the exact time-dependent density for the Moshinsky atom (initially in its ground-state) from

$$n(\mathbf{r}, t) = 2 \int |\psi_{\text{cm}}((\mathbf{r} + \mathbf{r}')/2, t) \psi_{\text{rm}}(\mathbf{r} - \mathbf{r}', t)|^2 d\mathbf{r}', \quad (54)$$

After straightforward analytical quadrature the result takes the form

$$n(\mathbf{r}, t) = 2 \left(\frac{\tilde{\mu}(t) \dot{\phi}_{\text{cm}}(t)}{\pi} \right)^{3/2} \exp \left(-\tilde{\mu}(t) \dot{\phi}_{\text{cm}}(t) r^2 \right), \quad (55)$$

where the purely time-dependent function $\tilde{\mu}(t)$ is given by

$$\tilde{\mu}(t) = \frac{2\dot{\phi}_{\text{rm}}(t)}{\dot{\phi}_{\text{cm}}(t) + \dot{\phi}_{\text{rm}}(t)}. \quad (56)$$

The correlated density matrix for this time dependent problem as defined by

$$\gamma(\mathbf{r}_1, \mathbf{r}_2, t) = 2 \int \psi^*(\mathbf{r}_1, \mathbf{r}, t) \psi(\mathbf{r}, \mathbf{r}_2, t) d\mathbf{r} \quad (57)$$

with

$$\psi(\mathbf{r}_1, \mathbf{r}_2, t) = \psi_{\text{cm}}((\mathbf{r}_1 + \mathbf{r}_2)/2, t) \psi_{\text{rm}}(\mathbf{r}_1 - \mathbf{r}_2, t), \tag{58}$$

is also available in closed form and reads

$$\begin{aligned} \gamma(\mathbf{r}_1, \mathbf{r}_2, t) = 2 \left(\frac{\tilde{\mu}(t) \dot{\phi}_{\text{cm}}(t)}{\pi} \right)^{3/2} \exp \left[-\tilde{\nu}(t) \dot{\phi}_{\text{cm}}(t) (r_1^2 + r_2^2) \right] \\ \times \exp \left[-\tilde{\eta}(t) \dot{\phi}_{\text{cm}}(t) (\mathbf{r}_1 + \mathbf{r}_2)^2 \right] \exp \left[i \delta(t) (r_1^2 - r_2^2) \right], \end{aligned} \tag{59}$$

where the following abbreviations have been employed:

$$\tilde{\nu}(t) = \frac{1}{4} \frac{(\dot{\phi}_{\text{cm}}(t) + \dot{\phi}_{\text{rm}}(t))^2 + (d \ln |X_{\text{rm}}(t)|/dt - d \ln |X_{\text{cm}}(t)|/dt)^2}{(\dot{\phi}_{\text{cm}}(t) + \dot{\phi}_{\text{rm}}(t)) \dot{\phi}_{\text{cm}}(t)} \tag{60}$$

$$\tilde{\eta}(t) = \frac{1}{4} (\tilde{\mu}(t) - 2\tilde{\nu}(t)) \tag{61}$$

$$\delta(t) = -\frac{1}{2} \frac{\dot{\phi}_{\text{cm}}(t) (d \ln |X_{\text{rm}}(t)|/dt) + \dot{\phi}_{\text{rm}}(t) (d \ln |X_{\text{cm}}(t)|/dt)}{\dot{\phi}_{\text{cm}}(t) + \dot{\phi}_{\text{rm}}(t)} \tag{62}$$

As evident from Eq. 59, the off diagonal elements of the correlated density matrix acquire a phase in the time dependent treatment. This also holds for the Dirac DM, which can be quite generally expressed as:

$$\gamma_s(\mathbf{r}_1, \mathbf{r}_2, t) = n(\mathbf{r}_1)^{1/2} n(\mathbf{r}_2)^{1/2} e^{i[f(\mathbf{r}_2,t) - f(\mathbf{r}_1,t)]}. \tag{63}$$

The phase arguments $f(\mathbf{r}, t)$ are directly related to the Kohn–Sham current and hence by means of the continuity equation also to the density [20]. We do not attempt to evaluate these terms here, but focus rather on the modulus of the density matrices. If we compare Eq. (55)/(59) with Eq. (37)/(38), we find that the time-dependent problem is completely equivalent to the time-independent one, provided we identify $\dot{\phi}_{\text{cm}}(t)$ with ω_0 and replace the exponents μ, ν with $\tilde{\mu}(t), \tilde{\nu}(t)$, respectively. Quite similar to Sect. 4.1, the time-dependent first order density matrix $\gamma(\mathbf{r}_1, \mathbf{r}_2, t)$ is then given in terms of the Dirac density matrix $\gamma_s(\mathbf{r}_1, \mathbf{r}_2, t)$

$$|\gamma(\mathbf{r}_1, \mathbf{r}_2, t)| = |\gamma_s(a(t) \mathbf{r}_1 + b(t) \mathbf{r}_2, b(t) \mathbf{r}_1 + a(t) \mathbf{r}_2)|, \tag{64}$$

with now time-dependent constants $a(t)$ and $b(t)$. Again, like in the static case, γ equals γ_s for vanishing inter-particle interaction.

5 Summary and outlook

The aim of the present article has been to generalize known DFT results to apply to TDDFT. Thus, we have established in Eq. 16 the result for the time-dependent

force $-\nabla V(\mathbf{r}, t)$, where $V(\mathbf{r}, t)$ is the central tool in current usage of TDDFT. This Eq. 16 is the generalization of the static analogue in Eq. 12 and involves the Dirac density matrix $\gamma_s(\mathbf{r}_1, \mathbf{r}_2, t)$ as central ingredient. For weak potentials, the diagonal of $\gamma_s(\mathbf{r}_1, \mathbf{r}_2, t)$ is sufficient to extract $V(\mathbf{r}, t)$. In Eq. 33, we report the explicit form of the time-dependent non-interacting response function which relates these two quantities.

We have also been concerned here with the specific example of the Moshinsky atom [34]. The central result is embodied in Eqs. 41 and 42 for the static limit, and in the dynamic generalization set out in Eq. 64. It would, of course, be of major interest for many-Fermion theory if it transpired that such relations between the correlated density matrix $\gamma(\mathbf{r}, \mathbf{r}')$ and the single-particle Dirac density matrix $\gamma_s(\mathbf{r}, \mathbf{r}')$ turned out to have more general applicability than for the Moshinsky model from which they have emerged.

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