

# Equation of motion of the correlated first-order density matrix for the ground-state of the Hookean atom with two electrons

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**Abstract** The ground-state wave function  $\Psi$  for a given force constant  $k = 1/4$  a.u. of the two-electron Hookean atom is known in exact analytical form. Here the corresponding first-order density matrix  $\gamma(\mathbf{r}, \mathbf{r}')$  is studied, particular attention being focussed on its equation of motion. The exact form which results from the known  $\Psi$  is displayed, and given a physical interpretation. Harmonic confined model two-electron atoms with arbitrary interaction  $u(r_{12})$  are also briefly referred to in the present context.

**Keywords** First-order density matrix · Equation of motion · Euler–Lagrange equation

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The study of the so-called Hookean atom with two electrons interacting with the Coulomb repulsion  $e^2/r_{12}$  goes back at the very least to the work of Kestner and Sinanoğlu [1]. The ground-state wave function  $\Psi(\mathbf{r}_1, \mathbf{r}_2)$  for the assumed harmonic confinement

$$V_{\text{ext}}(r) = \frac{1}{2}kr^2 \tag{1}$$

is known for  $k = \frac{1}{4}$  a.u. as [2]

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = C \exp(-|\mathbf{r}_1 + \mathbf{r}_2|^2/8) \exp(-|\mathbf{r}_2 - \mathbf{r}_1|^2/8), \tag{2}$$

where  $C = 1/[2\pi^{5/4}(5\pi^{1/2} + 8)^{1/2}] = 0.029112$  a.u.

Here, we are interested specifically in the first-order density matrix (1DM)  $\gamma(\mathbf{r}', \mathbf{r}'')$  corresponding to the wave function  $\Psi$  in Eq. (2) as defined by Löwdin [3–5]. A convenient form written by Qian and Sahni [6] is given by

$$\begin{aligned} \gamma(\mathbf{r}', \mathbf{r}'') &= 2C^2 \exp\left(-\frac{1}{4}(r'^2 + r''^2)\right) \\ &\int d\mathbf{r} \left(1 + \frac{1}{2}|\mathbf{r}' - \mathbf{r}|\right) \left(1 + \frac{1}{2}|\mathbf{r}'' - \mathbf{r}|\right) e^{-r^2/2}. \end{aligned} \tag{3}$$

To motivate what follows, let us refer here to the early work of March and Young [7]. For a given one-body potential  $V(x)$ , these authors wrote, with  $\gamma_s(x', x'')$  denoting their single particle ( $s$ ) idempotent 1DM, the following equation of motion

$$\frac{\partial^2 \gamma_s}{\partial x'^2} - \frac{\partial^2 \gamma_s}{\partial x''^2} = \frac{2m}{\hbar^2} [V(x') - V(x'')] \gamma_s. \tag{4}$$

This leads us, below, but now for the correlated 1DM  $\gamma(\mathbf{r}', \mathbf{r}'')$  given by Eq. (3), to focus on the ratio  $R(\mathbf{r}', \mathbf{r}'')$  defined by

$$R(\mathbf{r}', \mathbf{r}'') = \frac{\nabla_{\mathbf{r}'}^2 \gamma - \nabla_{\mathbf{r}''}^2 \gamma}{\gamma(\mathbf{r}', \mathbf{r}'')}. \tag{5}$$

Evidently, by insertion of the exact Hookean (H) form Eq. (3) into Eq. (5), the constant goes out and we find

$$R_H(\mathbf{r}', \mathbf{r}'') = [V_{\text{ext}}(\mathbf{r}') - V_{\text{ext}}(\mathbf{r}'') + F(\mathbf{r}', \mathbf{r}'')], \tag{6}$$

where  $R_H(\mathbf{r}', \mathbf{r}'')$  has been calculated explicitly from Eqs. (5) and (3) above as

$$R_H(\mathbf{r}', \mathbf{r}'') = \frac{1}{2} \frac{\int d\mathbf{r} e^{-r^2/2} \left[ \left(1 + \frac{1}{2}|\mathbf{r}'' - \mathbf{r}|\right) f(\mathbf{r}, \mathbf{r}') - f(\mathbf{r}, \mathbf{r}'') \left(1 + \frac{1}{2}|\mathbf{r}' - \mathbf{r}|\right) \right]}{\int d\mathbf{r} \left(1 + \frac{1}{2}|\mathbf{r}' - \mathbf{r}|\right) \left(1 + \frac{1}{2}|\mathbf{r}'' - \mathbf{r}|\right) e^{-r^2/2}}, \tag{7}$$

the function  $f(\mathbf{r}, \mathbf{r}')$  being given by

$$f(\mathbf{r}, \mathbf{r}') = \frac{2}{|\mathbf{r}' - \mathbf{r}|} - \frac{1}{2} \frac{(\mathbf{r}' - \mathbf{r}) \cdot \mathbf{r}'}{|\mathbf{r}' - \mathbf{r}|} - r'^2 - 3. \quad (8)$$

The very recent study of Amovilli and March [8] gives for  $R(\mathbf{r}', \mathbf{r}'')$  in Eq. (5) the general result

$$R(\mathbf{r}', \mathbf{r}'') = \frac{2m}{\hbar^2} [V(\mathbf{r}') - V(\mathbf{r}'') + g(\mathbf{r}', \mathbf{r}'')]. \quad (9)$$

Here,  $V(\mathbf{r})$  is the one-body potential of density functional theory (DFT) [9], which appears because in Eq. (5) the general correlated 1DM  $\gamma(\mathbf{r}', \mathbf{r}'')$  is expanded in the complete set of normalized Slater-Kohn-Sham [10, 11] orbitals  $\psi_i(\mathbf{r})$  generated by  $V(\mathbf{r})$  above as

$$\gamma(\mathbf{r}', \mathbf{r}'') = \sum_{ij} n_{ij} \psi_i(\mathbf{r}') \psi_j^*(\mathbf{r}''). \quad (10)$$

As shown in [8], only the off-diagonal occupation numbers  $n_{ij}$ ,  $i \neq j$ , enter  $g(\mathbf{r}', \mathbf{r}'')$  and, in general, for atoms, molecules and clusters, these can be expected to be small compared to the diagonal elements  $n_{ii}$ . In fact, for the example of the Hookean atom with  $k = 1/4$ , the DFT potential  $V(\mathbf{r}) \equiv V(|\mathbf{r}|)$  has already been determined in the work of Kais et al. [12].

Let us conclude by referring to the general treatment of Holas, Howard and March (HHM) [13] of the model two-electron atom, again with harmonic confinement given by Eq. (1), but now with general interparticle interaction  $u(r_{12})$ . The ground-state spatial wave function  $\Psi(\mathbf{r}_1, \mathbf{r}_2)$  takes the form of a product of a centre-of-mass (CM) contribution  $\psi_{\text{CM}}(\mathbf{r}_1, \mathbf{r}_2)$  and a relative motion ( $r$ ) part  $\psi_r(\mathbf{r}_1, \mathbf{r}_2)$ , that is

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_{\text{CM}}(|\mathbf{R}|) \psi_r(\mathbf{r}_1 - \mathbf{r}_2). \quad (11)$$

The CM term has the explicit form (with  $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$ )

$$\psi_{\text{CM}}(R) = \frac{1}{a_{\text{CM}}^{3/2} \pi^{3/4}} \exp\left(-\frac{1}{2} \frac{R^2}{a_{\text{CM}}^2}\right), \quad (12)$$

where

$$a_{\text{CM}}^{3/2} = \left(\frac{k}{2m\omega_0}\right)^{1/2}, \quad (13)$$

with  $\omega_0 = kR/m$  for constant  $k$  in Eq. (1).

The ground-state electron density  $\rho(\mathbf{r}_1)$  obtained by HHM [13] is given in terms of quadrature involving the relative motion wave function by

$$\rho(\mathbf{r}_1) = \frac{8}{\pi^{1/2}} e^{-r_1^2/a_{CM}^2} \int_0^\infty dy y^2 e^{-y^2/4} |\psi_r(a_{CM}y)|^2 \frac{\sinh(r_1y/a_{CM})}{r_1y/a_{CM}}. \tag{14}$$

The normalization factor  $\int d^3\mathbf{r}_1 \rho(\mathbf{r}_1) = 1$  is readily verified from Eq. (14). Fig. 1 of HHM [13] confirms that Eq. (14) agrees with the known Hookean atom density when  $u(r_{12}) = e^2/r_{12}$ .

The off-diagonal form of  $\rho(\mathbf{r})$ , viz. the exact correlated 1DM obtained in [13], is also characterized by the relative motion wave function, which satisfies a radial Schrödinger equation with effective one-body potential given by [13]

$$V_{\text{eff}}(r) = \frac{1}{2} m_r \omega_0^2 r^2 + u(r). \tag{15}$$

The 1DM has the explicit form in terms of  $\psi_{CM}$  and  $\psi_r$  as [13]

$$\begin{aligned} \gamma_1(\mathbf{r}_1, \mathbf{r}'_1) &= 2 \int d\mathbf{x} \psi_{CM} \left( \left| \frac{1}{2} \left( \mathbf{x} + 2\mathbf{c} + \frac{1}{2}\mathbf{b} \right) \right| \right) \psi_{CM} \left( \left| \frac{1}{2} \left( \mathbf{x} + 2\mathbf{c} - \frac{1}{2}\mathbf{b} \right) \right| \right) \\ &\times \psi_r \left( \left| \mathbf{x} - \frac{1}{2}\mathbf{b} \right| \right) \psi_r \left( \left| \mathbf{x} + \frac{1}{2}\mathbf{b} \right| \right). \end{aligned} \tag{16}$$

Here,  $\mathbf{b} = \mathbf{r}_1 - \mathbf{r}'_1$ ,  $\mathbf{c} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}'_1)$ ,  $\mathbf{x} = \mathbf{r}_2 - \mathbf{c}$ . The angular integration is performed in Eq. (16) but the result is complicated [13].

Let us now conclude by returning to the Hookean atom. Then Eq. (37) of [13] can be written in the form, for this special case of  $u(r_{12}) = e^2/r_{12}$ , as

$$\frac{\gamma(\mathbf{r}_1, \mathbf{r}'_1)}{\gamma(0, 0)} = \frac{\Psi(\mathbf{r}_1, \mathbf{r}'_1)}{\Psi(0, 0)} \chi(\mathbf{r}_1, \mathbf{r}'_1), \tag{17}$$

where the function  $\chi(\mathbf{r}_1, \mathbf{r}'_1)$  is determined only by  $\psi_{CM}(\mathbf{R})$  plus  $\chi(0, 0) = 1$ .

Thus, the part of the 2DM involved in the Dawson-March (DM) integrodifferential equation for  $\gamma(\mathbf{r}_1, \mathbf{r}'_1)$ , viz.  $\Gamma(\mathbf{r}_1, \mathbf{r}_1, \mathbf{r}'_1, \mathbf{r}_2)$ , is evidently given, for the two-electron Hookean atom, by

$$\Gamma(\mathbf{r}_1, \mathbf{r}_1, \mathbf{r}'_1, \mathbf{r}_2) = \Psi(\mathbf{r}_1, \mathbf{r}_1) \Psi(\mathbf{r}'_1, \mathbf{r}_2) = \frac{\gamma(\mathbf{r}_1, \mathbf{r}_2)}{\gamma(0, 0)} \frac{\Psi(0, 0)}{\chi(\mathbf{r}_1, \mathbf{r}_2)} \cdot \frac{\gamma(\mathbf{r}'_1, \mathbf{r}_2)}{\gamma(0, 0)} \frac{\Psi(0, 0)}{\chi(\mathbf{r}'_1, \mathbf{r}_2)}. \tag{18}$$

But from Eq. (2),  $\Psi(0, 0) = C$ , and hence

$$\Gamma(\mathbf{r}_1, \mathbf{r}_1, \mathbf{r}'_1, \mathbf{r}_2) = \frac{C^2}{\chi(\mathbf{r}_1, \mathbf{r}_2) \chi(\mathbf{r}'_1, \mathbf{r}_2)} \gamma(\mathbf{r}_1, \mathbf{r}_2) \gamma(\mathbf{r}'_1, \mathbf{r}_2), \tag{19}$$

where it is again to be noted that  $\chi(\mathbf{r}_1, \mathbf{r}_2)$  is determined solely by the analytically known centre-of-mass wave function given as proportional to  $\exp(-|\mathbf{r}_1 + \mathbf{r}_2|^2/8)$  in Eq. (2) above.

What is therefore remarkable to us is that, for the Hookean atom, the DM Euler–Lagrange (EL) equation for the correlated 1DM  $\gamma(\mathbf{r}_1, \mathbf{r}_2)$  closes, to read [14]

$$-\frac{\hbar^2}{2m} (\nabla_{\mathbf{r}_1}^2 - \nabla_{\mathbf{r}_2}^2) \gamma(\mathbf{r}_1, \mathbf{r}_2) + [V_{\text{ext}}(\mathbf{r}_1) - V_{\text{ext}}(\mathbf{r}_2)]\gamma(\mathbf{r}_1, \mathbf{r}_2) + \int d\mathbf{r} [u(|\mathbf{r}_1 - \mathbf{r}|) - u(|\mathbf{r}_2 - \mathbf{r}|)] \Gamma(\mathbf{r}_1, \mathbf{r}, \mathbf{r}_2, \mathbf{r}) = 0. \quad (20)$$

Inserting Eq. (19) into Eq. (20) then yields as an integrodifferential EL equation for the correlated 1DM the closed equation

$$-\frac{\hbar^2}{2m} (\nabla_{\mathbf{r}_1}^2 - \nabla_{\mathbf{r}_2}^2) \gamma(\mathbf{r}_1, \mathbf{r}_2) + [V_{\text{ext}}(\mathbf{r}_1) - V_{\text{ext}}(\mathbf{r}_2)]\gamma(\mathbf{r}_1, \mathbf{r}_2) + \int d\mathbf{r} [u(|\mathbf{r}_1 - \mathbf{r}|) - u(|\mathbf{r}_2 - \mathbf{r}|)] \frac{C^2}{\chi(\mathbf{r}_1, \mathbf{r})\chi(\mathbf{r}_2, \mathbf{r})} \gamma(\mathbf{r}_1, \mathbf{r})\gamma(\mathbf{r}_2, \mathbf{r}) = 0, \quad (21)$$

where  $\chi$  is determined solely by  $\psi_{\text{CM}}(\mathbf{R})$ .

There is, of course, extreme similarity to the Hartree-Fock method in Eq. (21). But equally important is the fact that Eq. (21) for the Hookean atom can now be compared with the formally exact result Eq. (6), for  $R_{\text{H}}$  defined by Eq. (5). Hence, for the Hookean (H) atom, the as yet unknown function  $F_{\text{H}}(\mathbf{r}_1, \mathbf{r}_2)$  is given from Eq. (21) by

$$F_{\text{H}}(\mathbf{r}_1, \mathbf{r}_2) = \frac{2m}{\hbar^2} \int d\mathbf{r} [u(\mathbf{r}_1 - \mathbf{r}) - u(\mathbf{r}_2 - \mathbf{r})] \frac{C^2}{\chi(\mathbf{r}_1, \mathbf{r})\chi(\mathbf{r}_2, \mathbf{r})} \frac{\gamma(\mathbf{r}_1, \mathbf{r})\gamma(\mathbf{r}_2, \mathbf{r})}{\gamma(\mathbf{r}_1, \mathbf{r}_2)}. \quad (22)$$

But, important for the connection with DFT emphasized above is the contact with the DFT potential  $V(\mathbf{r})$  appearing in Eq. (9). This potential, as mentioned above, is already known for the Hookean atom for force constant  $k = 1/4$  a.u. from the early study of Kais et al. [12]. Hence, an expression can be extracted for the function  $g(\mathbf{r}', \mathbf{r}'')$  appearing in Eq. (9).

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