Comment on "Response calculations with an independent particle system with an exact one-particle density matrix"

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Giesbertz, Gritsenko and Baerends (GGB) have stated that the occupation numbers n_k in time-dependent density matrix functional theory are time independent in the "adiabatic" approximation (AA) for *any* ground-state functional [1] (see also [2]). It is important to know whether this statement is true as it has implications for the design of functionals capable of generating time-dependent occupation numbers. Here we show that the argument given by GGB to support this statement is incorrect. The statement, however, is true; it follows quite generally from the stationarity of the ground state [3].

The equation of motion for the one-body reduced density matrix γ implies $idn_k/dt = W_{kk}^\dagger - W_{kk}$ [2], where

$$W_{kl} = \sum_{qrs} w_{kqrs}\Gamma_{srql} \tag{1}$$

with $\Gamma_{srql} = \langle\Psi|\hat{c}_l^\dagger \hat{c}_q^\dagger \hat{c}_r \hat{c}_s|\Psi\rangle$ and

$$w_{kqrs} \equiv \int dxdx' \phi_k^*(x)\phi_q^*(x')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_r(x')\phi_s(x). \tag{2}$$

In the AA, the memory-dependent functional $\Gamma([\gamma];t)$ on the right-hand side of Eq. (1) is approximated by the ground-state functional $\Gamma_0[\gamma]$ evaluated for $\gamma(t)$. GGB argue that the invariance of the ground-state interaction energy functional $W_0 = W_0[\gamma]$ with respect to the change $\phi_k \to e^{i\alpha_k}\phi_k$ in the phases of the natural orbitals implies $dn_k/dt = 0$. Therefore, they claim to prove the implication $dW_0[\gamma]/d\alpha_k = 0 \Rightarrow dn_k/dt = 0$. The crux of their argument is the statement

$$\frac{dW_0[\gamma]}{d\alpha_k} = W_{0,kk}^\dagger - W_{0,kk}, \tag{3}$$

where $W_{0,kk}$ are defined in the same way as the W_{kk} but with ground-state quantities. To establish Eq. (3), GGB use the identity

$$i\frac{dW_0}{d\alpha_k} = \int dx \frac{\delta W_0}{\delta\phi_k^*(x)}\phi_k^*(x) - \int dx\frac{\delta W_0}{\delta\phi_k(x)}\phi_k(x) \tag{4}$$

and the statement

$$W_{0,kk}^\dagger = \int dx\frac{\delta W_0}{\delta\phi_k^*(x)}\phi_k^*(x), \tag{5}$$

quoted from Ref. 4, where it was derived from

$$\frac{\delta W_0[\gamma]}{\delta\phi_i^*(x)} = \sum_p \frac{\partial W_0[\gamma]}{\partial\xi_p}\frac{\delta\xi_p}{\delta\phi_i^*(x)} + \frac{1}{2}\sum_{kqrs}\frac{\delta w_{kqrs}}{\delta\phi_i^*(x)}\Gamma_{srqk}. \tag{6}$$

Here $W_0[\gamma] = \frac{1}{2}\min_{\{\xi_p\}}\sum_{kqrs} w_{kqrs}\Gamma_{srqk}(\xi_p)$ and $\{\xi_p\}$ parametrize a constrained search over N-representable Γ_{srqk} that contract to γ. It was argued [4] that Eq. (5) follows from Eq. (6) because the first term vanishes due to the variational nature of the constrained search. But there are two flaws with this argument: (i) Eq. (6) itself is manifestly incorrect because $W_0[\gamma]$ has no $\{\xi_p\}$ dependence after the constrained search has been performed: the operations $\sum_p \frac{\partial}{\partial\xi_p}$ and $\min_{\{\xi_p\}}$ do not commute; (ii) The variational character of $W_0([\phi_i];\xi_p) \equiv \frac{1}{2}\sum_{kqrs} w_{kqrs}\Gamma_{srqk}(\xi_p)$ at the minimizing ξ_p for fixed $\{\phi_i, n_i\}$ does not imply that the gradient with respect to ξ_p is zero, because $W_0([\phi_i];\xi_p)$ is only stationary with respect to the subspace of $\{\xi_p\}$ degrees of freedom that are orthogonal to the ϕ_i degrees of freedom as the latter are *constrained*. Ultimately, the argument is incorrect because it does not account for the ϕ_i dependence of Γ_{srqk}.

For the specific case of approximate $W_0[n_i, \phi_i, \phi_i^*]$ that contain only w_{kqkq} and w_{kqqk} Coulomb integrals and in which the Γ_{srqk} are functions of n_i, it might seem that Eq. (5) can be verified by an explicit calculation of the functional derivative. However, such a calculation is not valid because the variation $\phi_k^* \to \phi_k^* + \delta\phi_k^*$ holding fixed all other ϕ_i^* and all ϕ_i corresponds to a non-Hermitian $\gamma + \delta\gamma$. Hence, such a variation goes outside the physical domain of $W_0[n_i, \phi_i, \phi_i^*]$. The functional derivative of $W_0[\gamma]$ with respect to an orbital should be understood as

$$\int dx\frac{\delta W_0[\gamma]}{\delta\phi_k^*(x)}\phi_k^*(x) = n_k \int dxdx' \phi_k^*(x)\frac{\delta W_0[\gamma]}{\delta\gamma(x',x)}\phi_k(x'), \tag{7}$$

where now $W_0[\gamma] = \frac{1}{2}\int dx_1 dx_2 \frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\Gamma_0([\gamma]; x_1x_2, x_1x_2)$ and $\Gamma_0([\gamma]; x_1x_2, x_1'x_2')$ is the ground-state two-body reduced density matrix functional [5]. Clearly, Eqs. (4) and (7) cannot justify Eq. (3) because the right-hand side of Eq. (3) depends on degrees of freedom of $\Gamma_0(x_1x_2, x_1'x_2')$ that are integrated out in the definition of $W_0[\gamma]$. This information cannot be recovered by taking the derivative with respect to α_k.

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