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1986 J. Phys. A: Math. Gen. 19 2549

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# The probability and energy density currents as density functionals

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Received 24 June 1985, in final form 28 October 1985

**Abstract.** Starting with a polar decomposition of the wavefunction, it is shown that the probability and energy density currents are explicit functionals of the probability and energy densities. At a non-reduced level and for a  $(n_1 + n_2)$ -particle system, the expression of these functionals is exactly calculated. This leads to a system of coupled equations equivalent to the Schrödinger equation. The probability and energy densities are unknown. Some properties of the functionals are analysed and the particular case of a one-body Hamiltonian studied.

## 1. Introduction

In a recent paper on the extension of the density functional approach (DFA) to time-dependent (TD) problems (for a general discussion on DFA, with many references, see Ghosh and Deb (1982)), Runge and Gross (RG) (1984) have demonstrated two theorems. Theorem 1 states the invertibility of the mapping between  $U(\mathbf{r}, t)$  and the density  $\rho(\mathbf{r}, t)$  for the TD Schrödinger equation:

$$\left(-\frac{\hbar^2}{2m}\Delta + \hat{U}(\mathbf{r}, t) - i\hbar\frac{\partial}{\partial t}\right)\psi(\mathbf{r}, t) = 0 \quad (1)$$

with  $\rho(\mathbf{r}, t) = \langle \psi(t) | \hat{\psi}^\dagger(\mathbf{r}) \hat{\psi}(\mathbf{r}) | \psi(t) \rangle$  and  $\hat{U}(\mathbf{r}, t)$  a single-particle TD potential on  $R^3$ .  $\hat{U}(\mathbf{r}, t)$  consists of an internal part which can be TD-like time-dependent Hartree-Fock (TDHF) potentials and eventually an external TD perturbative part.

Theorem 2 states the existence of a mapping between  $\rho(\mathbf{r}, t)$  and the associated current density  $\mathbf{J}(\mathbf{r}, t)$ , i.e.  $\mathbf{J}(\mathbf{r}, t) = \mathbf{Q}(\rho(\mathbf{r}, t))$  with  $\mathbf{Q}$  a functional to be determined.

Xu and Rajagopal (1985) have already commented on the demonstration given by RG for theorem 1 and on the fact that for a given initial  $\rho(\mathbf{r}, t_0)$  only the mapping  $\mathbf{J}(\mathbf{r}, t) = \mathbf{P}(U(\mathbf{r}, t))$  can be explicitly inverted, not  $\mathbf{J}(\mathbf{r}, t) = \mathbf{Q}(\rho(\mathbf{r}, t))$ .

We comment here in two steps on theorem 2. First, we demonstrate, for a stable inhomogeneous quantum system ( $S$ ) of  $n_1$  electrons and  $n_2$  nuclei, that even at the many-body level (i.e. when the densities like  $\rho$  are defined on the entire configuration space and then called non-reduced densities)  $\mathbf{J}_\rho$  is not only a  $\rho$  functional. The choice of the non-reduced level (NR) enables us to obtain the exact expression of each TD density functional and to demonstrate their equivalence with the TD( $n_1 + n_2$ ) Schrödinger equation.

The first step is divided into two parts. In § 2, we recall the Madelung decomposition and introduce the energy density  $\varepsilon$  and its associated current  $\mathbf{J}_\varepsilon$ . In § 3, we give the

exact expression of the functional  $J_\rho = J_\rho(\rho, \varepsilon)$  and  $J_\varepsilon = J_\varepsilon(\rho, \varepsilon)$ , and demonstrate their equivalence with the Schrödinger equation.

In a second step (§ 4), we apply these results to the analysis of the  $J_\rho$  and  $J_\varepsilon$  functional properties and to give a condition such that  $J_\rho$  is a TD functional of the densities  $\rho$  and  $\varepsilon$ . Finally, we study the TD potential case at the reduced level.

In §§ 2 and 3, only time-independent (TI) potentials are considered. The TD evolution regime is then induced by a non-stationary initial-state excitation. This choice is based on the fact that for the internal part of the potential in the Hamiltonian, one goes from TI potentials on the configuration space to TD potentials on  $R^3$  by truncation of the BBGKY hierarchy as in TDHF. Therefore DFA must be the same in the TI and TD cases.

**2. The energy densities  $\varepsilon$  and  $J_\varepsilon$**

On the configuration space ( $C_S$ ), the wavefunction  $\psi(X_{11} \dots X_{1n_1}, X_{21} \dots X_{2n_2}, t)$  of  $S$  is the solution of the Schrödinger equation

$$(\hat{H} - i\hbar \partial/\partial t)\psi(\hat{X}_{\alpha k}, t) = 0 \tag{2}$$

with the  $X_{1k}$  ( $k = 1, n_1$ ) electron and the  $X_{2k}$  ( $k = 1, n_2$ ) nucleus coordinates.

The Hamiltonian  $\hat{H}$  is written as usual

$$\hat{H} = \sum_{\beta=1}^2 \sum_{j=1}^{n_\beta} \frac{-\hbar^2}{2m_{\beta j}} \Delta_{\beta j} + \hat{W}(X_{\alpha k}) \tag{3}$$

where  $\hat{W}(X_{\alpha k})$  is the TI Coulombic potential between the  $n_1 + n_2$  particles considered in  $S$ , and  $m_{\beta j}$  their respective mass.

We know that one way to DFA at the NR level is to substitute  $\psi(X_{\alpha k}, t)$  in (2) with its polar decomposition form (Ghosh and Deb 1982). This substitution, usually called the Madelung decomposition (Madelung 1926), gives the set of two coupled equations

$$\hbar \frac{\partial \phi}{\partial t} = \sum_{\beta=1}^2 \sum_{j=1}^{n_\beta} \frac{-\hbar^2}{2m_{\beta j}} (2\nabla_{\beta j} \phi \cdot \nabla_{\beta j} \theta + \phi \Delta_{\beta j} \theta) \tag{4}$$

$$-\hbar \frac{\partial \theta}{\partial t} = \sum_{\beta=1}^2 \sum_{j=1}^{n_\beta} \frac{-\hbar^2}{2m_{\beta j}} [\Delta_{\beta j} \phi - \phi (\nabla_{\beta j} \theta \cdot \nabla_{\beta j} \theta)] + W(X_{\alpha k}) \phi. \tag{5}$$

In (4) and (5) the polar decomposition of  $\psi(X_{\alpha k}, t)$  has been taken as

$$\psi(X_{\alpha k}, t) = \phi(X_{\alpha k}, t) \exp i\theta(X_{\alpha k}, t) \tag{6}$$

with  $\phi$  and  $\theta$  two real valued functions on  $C_S \times R$ , solutions of (4) and (5) for a given initial condition  $\psi(X_{\alpha k}, t_0)$ .  $\phi$  and  $\theta$  must also verify the conditions  $\int \psi(X_{\alpha k}, t) \psi^*(X_{\alpha k}, t) d\tau = 1$  for the module part  $\phi$  and  $\int \psi^*(X_{\alpha k}, t) H \psi(X_{\alpha k}, t) d\tau = E$  for the phase part  $\theta$  with  $E$  the internal energy of  $S$ .

After some calculations, equation (4) gives the classical probability conservation law:

$$(\partial/\partial t) \rho + \text{div}(J_\rho) = 0 \tag{7}$$

with

$$\rho = \rho(X_{\alpha k}, t) = \phi^2(X_{\alpha k}, t) \tag{8}$$

$$J_\rho = J_\rho(X_{\alpha k}, t) = \hbar \rho(X_{\alpha k}, t) M^{-1} \cdot \text{grad}(\theta(X_{\alpha k}, t)) \tag{9}$$

and

$$\text{grad} = (\nabla_{11}, \dots, \nabla_{1n_1}, \nabla_{21}, \dots, \nabla_{2n_2})$$

$$\text{div} = \sum_{\beta=1}^2 \sum_{j=1}^{n_\beta} \nabla_{\beta j}.$$

$M^{-1}$  is the inverse diagonal mass matrix with  $m_{kk} = m_{1k}$  for  $k = 1, n$  and  $m_{kk} = m_{2k}$  for  $k = n_1 + 1, n_1 + n_2$ .

The factorisation in (5) of the  $C_S$  velocity  $V$  defined by its 'vectorial components'  $V_{\beta j} = \hbar m_{jj}^{-1} \nabla_{\beta j} \theta(\mathbf{X}_{\alpha k}, t)$  leads to the usual hydrodynamic equation

$$\frac{\partial}{\partial t} (M \cdot V) + \frac{1}{2} M \cdot \text{grad}(\|V\|^2) = -\text{grad}(g) \tag{10}$$

with  $g = g(\mathbf{X}_{\alpha k}, t)$  a real valued function on  $C_S \times R$  defined by

$$g(\mathbf{X}_{\alpha k}, t) = (\hat{H}\rho^{1/2}(\mathbf{X}_{\alpha k}, t))\rho^{1/2}(\mathbf{X}_{\alpha k}, t). \tag{11}$$

At this stage, everything is in agreement with the hydrodynamic formalism on  $C_S \times R$ . Beginning with the set of unknown functions  $(\phi, \theta)$  on  $C_S \times R$ , we arrive at the set  $(\rho, V)$  in (7) and (10) or at the set  $(\rho, J_\rho)$  also on  $C_S \times R$ . However, the last two sets have an 'inhomogeneous' composition of one scalar and one vectorial function. Therefore, it is not possible to decompose  $J_\rho$ , at least on  $\rho$ , to extract the response coefficients of  $S$  to a non-stationary initial excitation.

The 'homogenisation' of the unknown set can be realised with an exchange of  $\rho$  by a vectorial, or  $J_\rho$  by a scalar, function. The second solution is more interesting in the context of the response analysis of  $S$ . However, in order to introduce a new set of unknown functions at the NR level, two conditions must be verified:

(a) the existence of a coupled equation system which determines the two functions of the set, and

(b) this system must be equivalent at the NR level to the Schrödinger equation (2).

By clustering the second left-hand term of (10) with  $g$ , equation (10) is rewritten with (9):

$$M \frac{\partial}{\partial t} \left( \frac{J_\rho}{\rho} \right) = -\text{grad} \left( \frac{\varepsilon}{\rho} \right). \tag{12}$$

The scalar real valued function  $\varepsilon = \varepsilon(\mathbf{X}_{\alpha k}, t)$  on  $C_S \times R$  is defined by

$$\varepsilon(\mathbf{X}_{\alpha k}, t) = g(\mathbf{X}_{\alpha k}, t) + \frac{1}{2} \rho^{-1}(\mathbf{X}_{\alpha k}, t) \| M^{1/2} \cdot J_\rho(\mathbf{X}_{\alpha k}, t) \|^2. \tag{13}$$

Following conditions (a) and (b), the set  $(\rho, \varepsilon)$  will be a useful set of unknown functions if

(c)  $\varepsilon$  represents an interesting physical quantity,

(d)  $J_\rho$  is an explicit  $(\rho, \varepsilon)$  functional, and

(e) there exists an equation other than (7), which governs the time and spatial evolution of  $\varepsilon$ , to close the system of equations.

For (c), it can be easily seen that  $\varepsilon$  has the dimension of an energy density. For example, if we take  $\psi(\mathbf{X}_{\alpha k}, t) = \phi_n(\mathbf{X}_{\alpha k}) \exp -(i/\hbar) E_n t$  with  $E_n$  a non-degenerate element of the discrete spectrum of  $\hat{H}$  and  $\phi_n$  the associated real valued eigenfunction,  $J_\rho = 0$  from (9) and  $\varepsilon = (\hat{H}\phi_n)\phi_n = E_n \rho$  from (13).

For (d), after a formal integration of (12), we obtain

$$J_\rho(t) = \rho(t)M^{-1} \cdot \int_0^t \text{grad}\left(\frac{\varepsilon(t')}{\rho(t')}\right) dt' \tag{14}$$

showing that  $J_\rho$  is a  $(\rho, \varepsilon)$  functional.

The direct demonstration of (d) without polar decomposition of the wavefunction and the study of (e) is dealt with in the next section. We need, first, to prove that  $\varepsilon$  given by (13) is equal to the energy density  $\frac{1}{2}[(H\psi)\psi^* + (H\psi)^*\psi]$  defined for example by Jauch (1968). Then the energy density current  $J_\varepsilon$  can be properly defined and the conservation equation of  $\varepsilon$  introduced in a natural way.

Beginning with the Lagrangian density associated with the wavefunction  $\psi(\mathbf{X}_{\alpha k}, t)$  written as usual (Schiff 1968):

$$\mathcal{L} = \left( \sum_{\beta=1}^2 \sum_{j=1}^{n_\beta} \frac{\hbar^2}{2m_{\beta j}} \nabla_{\beta j} \psi^* \cdot \nabla_{\beta j} \psi + \hat{W}(\mathbf{X}_{\alpha k}) \psi \psi^* \right) - i\hbar \left( \psi^* \frac{\partial \psi}{\partial t} - \psi \frac{\partial \psi^*}{\partial t} \right) \tag{15}$$

and for an infinitesimal transformation  $T_{\Delta t}(\psi(\mathbf{X}_{\alpha k}, t)) = \psi(\mathbf{X}_{\alpha k}, t + \Delta t)$ , the Noether theorem leads to the energy conservation equation (see Gaudin (1967) and for a topological analysis Westhenholz (1979))

$$(\partial/\partial t) I - \text{div } \mathbf{J} = 0 \tag{16}$$

with

$$I = \mathcal{L} - \left( \frac{\partial \mathcal{L}}{\partial \psi_t} \right) \psi_t - \left( \frac{\partial \mathcal{L}}{\partial \psi_t^*} \right) \psi_t^* \tag{17}$$

and for a  $J_{\beta j}$  component of  $\mathbf{J}$ :

$$J_{\beta j} = - \left( \frac{\partial \mathcal{L}}{\partial \psi_{\beta j}} \right) \psi_t - \left( \frac{\partial \mathcal{L}}{\partial \psi_{\beta j}^*} \right) \psi_t^* \tag{18}$$

$\beta$  indexes the particle,  $j$  its coordinates on  $C_S$ ,  $\psi_t = \partial \psi / \partial t$  and  $\psi_{\beta j} = \partial \psi / \partial x_{\beta j}$ .

With symmetrical decomposition of the term  $\nabla_{\beta j} \psi^* \cdot \nabla_{\beta j} \psi$  in (15), the calculation of (17) and (18) is straightforward and it comes from (16):

$$\frac{\partial}{\partial t} \left\{ \frac{1}{2} [(\hat{H}\psi)^*\psi + (\hat{H}\psi)\psi^*] \right\} + \text{div}(\mathbf{J}_\varepsilon) = 0 \tag{19}$$

with  $\mathbf{J}_\varepsilon = \mathbf{J}_\varepsilon(\mathbf{X}_{\alpha k}, t)$  a real valued vectorial function defined on  $C_S \times R$  and equal to

$$\mathbf{J}_\varepsilon = \frac{1}{2} \hbar^2 M^{-1} \cdot \left( \psi \frac{\partial}{\partial t} (\text{grad } \psi)^* - (\text{grad } \psi) \frac{\partial}{\partial t} \psi^* + \psi^* \frac{\partial}{\partial t} (\text{grad } \psi) - (\text{grad } \psi)^* \frac{\partial}{\partial t} \psi \right) \tag{20}$$

which is equal to the energy density current defined by Jauch.

The vectorial function  $\mathbf{J}$  in (16) is not equal to  $\mathbf{J}_\varepsilon$ . In fact from (17) and (18) two factorisations are possible: equation (16) or equation (19). However, only equation (19) leads to densities, like the densities  $\rho$  and  $J_\rho$  in (7), corresponding to field operator averages. For example

$$\frac{1}{2} [(\hat{H}\psi)^*\psi + (\hat{H}\psi)\psi^*] = \langle \psi(t) | \frac{1}{2} [\hat{H}, \hat{\psi}^+(X_{11}) \dots \hat{\psi}^+(X_{2n_2}) \hat{\psi}(X_{11}) \dots \hat{\psi}(X_{2n_2})] | \psi(t) \rangle \tag{21}$$

which is certainly not the case for  $I$  in (16).

We demonstrate now that the density  $\varepsilon$  obtained in (12) is equal to the energy density defined by Jauch. The polar decomposition of  $\psi$  gives

$$\hat{H}\psi = e^{i\theta} \left( \sum_{\beta=1}^2 \sum_{j=1}^{n_{\beta}} \frac{-\hbar^2}{2m_{\beta j}} [\Delta_{\beta j} \phi + 2i(\nabla_{\beta j} \phi \cdot \nabla_{\beta j} \theta) + i\phi \Delta_{\beta j} \theta - \phi(\nabla_{\beta j} \theta \cdot \nabla_{\beta j} \theta)] + \hat{W}(X_{\alpha k}) \phi \right). \tag{22}$$

Then

$$\frac{1}{2}[(\hat{H}\psi)^* \psi + (\hat{H}\psi)\psi^*] = \phi \left( \sum_{\beta=1}^2 \sum_{j=1}^{n_{\beta}} \frac{-\hbar^2}{2m_{\beta j}} \Delta_{\beta j} \phi + \hat{W}(X_{\alpha k}) \phi \right) + \sum_{\beta=1}^2 \sum_{j=1}^{n_{\beta}} \frac{\hbar^2}{2m_{\beta j}} \phi^2 (\nabla_{\beta j} \theta \cdot \nabla_{\beta j} \theta) \tag{23}$$

which is equal to  $\varepsilon$  from (9) and (11).

### 3. Equivalence between $(\rho, \varepsilon)$ and $\psi$ at the NR level

In the last section,  $\varepsilon$  and  $J_{\varepsilon}$  were obtained from hydrodynamical equations (7) and (10) which are evolution equations of  $(\rho, J_{\rho})$  or  $(\rho, \mathbf{V})$ . From condition (a), two new coupled equations in  $\rho$  and  $\varepsilon$  are needed to use  $(\rho, \varepsilon)$  as an unknown set of functions.

One of these two equations has already been derived because, with (14) substituted in (7), we obtain

$$\frac{\partial}{\partial t} \rho + \text{div} \left[ \rho M^{-1} \cdot \int_0^t \text{grad} \left( \frac{\varepsilon(t')}{\rho(t')} \right) dt' \right] = 0 \tag{24}$$

which is only a  $(\rho, \varepsilon)$  equation.

Because we have proved that  $\varepsilon$  is equal to (21), the development of  $J_{\rho}$  on  $(\rho, \varepsilon)$  used to derive (24) can be obtained without polar decomposition. From the usual definition of  $J_{\rho}$  comes

$$J_{\rho} = \frac{\hbar}{2i} \rho M^{-1} \cdot \text{grad}(\log \psi - \log \psi^*) \tag{25}$$

or

$$J_{\rho} = \frac{\hbar}{2i} \rho M^{-1} \cdot \text{grad} \left( \int_0^t \psi(t')^{-1} \frac{\partial \psi(t')}{\partial t'} - \psi(t')^{-1*} \frac{\partial}{\partial t'} \psi(t')^* dt' \right) \tag{26}$$

and the development (14) of  $J_{\rho}$  on  $(\rho, \varepsilon)$  is found again with (2) in (26). It is also interesting to note that  $J_{\rho}$  depends on the gradient of  $\rho$  because (14) can be developed as

$$J_{\rho} = \left( \int_0^t \frac{\varepsilon(t')}{\rho(t')} dt' \right) M^{-1} \cdot \text{grad} \rho - \left( \frac{\rho}{\varepsilon} \int_0^t \frac{\varepsilon(t')}{\rho(t')} dt' \right) M^{-1} \cdot \text{grad} \varepsilon - \varepsilon M^{-1} \cdot \text{grad} \left( \frac{\rho}{\varepsilon} \int_0^t \frac{\varepsilon(t')}{\rho(t')} dt' \right). \tag{27}$$

The  $J_{\rho}$  functional does not follow the Fourier law  $J_{\rho} = \alpha \text{grad} \rho$  proposed recently by Ioannidou (1983). The coefficients of  $\text{grad} \rho$  and  $\text{grad} \varepsilon$  are TD at the NR level and  $J_{\rho}$  is non-linear in  $(\rho, \varepsilon)$ .

The second equation must be constructed with conservation equation (19) because the dynamic (10) and the conservation (7) equation have already been used to derive (24). From (20),  $J_e$  is rewritten

$$J_e = \frac{1}{4}\hbar^2 \psi \psi^* M^{-1} \cdot \left( \frac{\psi}{\psi^*} \text{grad} \frac{(\partial/\partial t)\psi^*}{\psi} + \frac{\psi^*}{\psi} \text{grad} \frac{(\partial/\partial t)\psi}{\psi^*} \right) \tag{28}$$

or with a polar decomposition of  $\psi$ :

$$J_e = \frac{1}{2}\hbar\rho M^{-1} \cdot \text{Im} \left[ e^{-2i\theta} \text{grad} \left( \frac{\psi(\hat{H}\psi)}{\rho} \right) \right]. \tag{29}$$

However,  $\hat{H}\psi$  has been already calculated in § 2 and the substitution of (22) in (29) gives

$$J_e = \frac{1}{2}\hbar\rho M^{-1} \cdot \left( \frac{2}{\hbar} \rho^{-2} M \cdot J_\rho (\varepsilon - \frac{1}{2}\rho^{-1} \|M^{1/2} \cdot J_\rho\|^2) + \frac{1}{\hbar} \rho^{-2} M \cdot J_\rho \rho^{-1} \|M^{1/2} \cdot J_\rho\|^2 - \frac{1}{2}\hbar \text{grad}(\rho^{-1} \text{div}(J_\rho)) \right) \tag{30}$$

or, after simplification,

$$J_e = \frac{J_\rho \varepsilon}{\rho} - \frac{1}{4}\hbar^2 \rho M^{-1} \cdot \text{grad} \left( \frac{1}{\rho} \text{div}(J_\rho) \right) \tag{31}$$

which is only a  $(\rho, \varepsilon)$  functional.

$J_e$  is composed of two terms: one ‘classical’, the energy current calculated from the speed  $J_\rho/\rho$ , and one purely quantum. The contribution of this term to  $J_e$  is greater according to the extent of the variation of  $J_\rho$ , normalised by  $\rho$ , on  $C_S$ .

As in  $J_\rho$  in (27),  $J_e$  can be developed as

$$J_e = \left( \int_0^t \frac{\varepsilon(t')}{\rho(t')} dt' \right) M^{-1} \cdot \text{grad} \varepsilon - \left( \frac{\varepsilon}{\rho} \int_0^t \frac{\varepsilon(t')}{\rho(t')} dt' \right) M^{-1} \cdot \text{grad} \rho - \rho M^{-1} \cdot \text{grad} \left( \frac{\varepsilon}{\rho} \int_0^t \frac{\varepsilon(t')}{\rho(t')} dt' \right) - \frac{\hbar^2}{4} M^{-1} \rho \cdot \text{grad} \left( \frac{1}{\rho} \text{div} J_\rho \right). \tag{32}$$

The  $J_e$  functional does not follow a Fourier law and is non-linear in  $\rho$  and  $\varepsilon$ .

The equation which completes (24) and fulfils conditions (a) and (e) can now be written using (13), (19), (23) and (32):

$$\frac{\partial \varepsilon}{\partial t} + \text{div} \left\{ \left[ \varepsilon M^{-1} \cdot \int_0^t \text{grad} \left( \frac{\varepsilon(t')}{\rho(t')} \right) dt' \right] - \frac{\hbar^2}{4} \rho M^{-1} \times \text{grad} \left\{ \frac{1}{\rho} \text{div} \left[ \rho M^{-1} \cdot \int_0^t \text{grad} \left( \frac{\varepsilon(t')}{\rho(t')} \right) dt' \right] \right\} \right\} = 0. \tag{33}$$

The equation system (7) and (19) is now closed. For a given initial condition  $\psi(t_0)$ , the equivalence of (2) with this system (condition (b)) follows from (32): for  $\varepsilon(t_0)$  and  $\rho(t_0)$  calculated from  $\psi(t_0)$ , the function  $\rho(t)$  and  $\varepsilon(t)$  solution of (24) and (33) lead directly from (14) to  $J_\rho(t)$  and from (9) to the phase  $\theta(t)$ . Finally, from  $\rho(t)$  and  $\theta(t)$ ,  $\psi(t)$  is reconstructed with  $\psi(t) = \rho^{1/2}(t) \exp i\theta(t)$ .

With this equivalence, the equivalence chain between all the possible sets of densities is completed:

$$\psi \Leftrightarrow (\psi, \psi^*) \Leftrightarrow (\phi, \theta) \Leftrightarrow (\rho, \mathbf{V}) \begin{matrix} \Leftrightarrow (\rho, \mathbf{J}_\rho) \\ \Downarrow \\ \Leftrightarrow (\rho, \varepsilon) \end{matrix} .$$

At the NR level  $(\rho, \mathbf{V})$  or  $(\rho, \mathbf{J}_\rho)$  are used to construct the hydrodynamic form of the Schrödinger equation.  $(\rho, \varepsilon)$  is more appropriate to characterise the intrinsic response of  $S$  to an excitation: if  $\rho$  and  $\varepsilon$  are taken as independent unknown functions,  $\mathbf{J}_\rho$  and  $\mathbf{J}_\varepsilon$  become the response functions of  $S$ .

The important parts in  $\mathbf{J}_\rho$  and  $\mathbf{J}_\varepsilon$  are the response coefficients which carry all the intrinsic physical properties of  $S$  in the range of its excitation. In this context, one use of  $(\rho, \varepsilon)$  for intramolecular behaviours like IVR (intramolecular vibrational relaxation) or ICT (intramolecular charge transfer) is to calculate energy and charge transfer (or diffusion) coefficients. For example,  $\varepsilon$  is a very useful function for taking account of non-adiabatic dynamic coupling, an important effect in IVR (Joachim 1984). Such behaviour is usually characterised, through a spectral decomposition of the wavefunction, by the associate Hamiltonian spectrum properties (Joachim 1985) which lead only to a trajectory-like classification: regular, stochastic or chaotic.

#### 4. Properties of the currents $\mathbf{J}_\rho$ and $\mathbf{J}_\varepsilon$

The first property we propose to discuss concerns the characteristic of the response of  $S$  starting from  $\text{grad}(\varepsilon/\rho)$ . Equation (12) leads to the following.

For a preparation in a stationary state,  $\varepsilon$  is proportional to  $\rho$ . The proportionality coefficient is a constant for TI potentials and the TD current does not exist. TI currents exist (vortexes for example) if the eigenfunction of the prepared stationary state is complex-valued.

For a preparation in a non-stationary state, the initial difference between  $\varepsilon$  and  $\rho$  governs the apparition of the TD currents  $\mathbf{J}_\rho$  and  $\mathbf{J}_\varepsilon$ .

The second property of  $\mathbf{J}_\rho$  and  $\mathbf{J}_\varepsilon$  involves the  $\text{grad} \rho$  and  $\text{grad} \varepsilon$  coefficients in (27) and (32). The decomposition of (14) and (31) in (27) and (32) was used to prove that  $\mathbf{J}_\rho$  and  $\mathbf{J}_\varepsilon$  are not of the Fourier type. But this decomposition also suggests an Onsager-like relation between the coefficients obtained.

In the linear response theory, the response coefficients are defined through the gradient of the  $\rho$  and  $\varepsilon$  conjugated variables. At the NR level, taking  $\varepsilon^{-1}$  and  $\rho^{-1}$  as the conjugated variables (which is *only* a convenient choice in relation with the unit of measurement of  $1/T$  and  $\mu/T$  at the statistical level), equations (27) and (32) become

$$\mathbf{J}_\alpha = \sum_{\beta} L_{\alpha\beta}(\rho, \varepsilon) \text{grad}(\beta^{-1}) + \mathbf{F}_\alpha(\rho, \varepsilon) \quad (34)$$

for  $\alpha = \varepsilon, \rho$ ,  $\beta = \varepsilon, \rho$  and

$$L_{\varepsilon\varepsilon} = -\varepsilon^2 K(\rho, \varepsilon) \quad (35a)$$

$$L_{\rho\rho} = -\rho^2 K(\rho, \varepsilon) \quad (35b)$$

$$L_{\varepsilon\rho} = L_{\rho\varepsilon} = \rho\varepsilon K(\rho, \varepsilon). \quad (35c)$$

The functionals  $K(\rho, \varepsilon)$  and  $\mathbf{F}_\alpha(\rho, \varepsilon)|_{\alpha=\rho,\varepsilon}$  are easily obtained from (27) and (32).



In the first-order development in powers of  $(\varepsilon/\rho)$  used to obtain (27) and (32), a reciprocal relation (35c) appears between the non-diagonal elements of  $L$ . However, it is not exactly the Onsager reciprocal relation, because we can continue to develop  $F_\alpha(\rho, \varepsilon)$  in powers of  $(\varepsilon/\rho)$  to obtain linear terms in  $\text{grad}(\varepsilon^{-1})$  and  $\text{grad}(\rho^{-1})$ . This development cannot be closed, but the equality (35c),  $L_{\varepsilon\varepsilon} < 0$  and  $L_{\rho\rho} < 0$ , are conserved to each order.

Another property, in relation to the last one, is that from (31) and whatever the initial preparation of  $S$ , if  $\mathbf{J}_\rho = 0$  then  $\mathbf{J}_\varepsilon = 0$ . The converse proposition is only true for a preparation in a stationary state.

Concerning the second RG theorem,  $\mathbf{J}_\rho$  and  $\mathbf{J}_\varepsilon$  are functionals of the densities only if the set  $(\rho, \varepsilon)$  is chosen. Let us examine, for example, the  $\mathbf{J}_\rho$  property proposed by RG for a TD one-body potential

$$(\partial/\partial t)\mathbf{J}_\rho(\mathbf{r}, t) = \mathbf{G}(\rho(\mathbf{r}, t)). \tag{36}$$

For TI one-body potentials, results in §§ 2 and 3 can be used. If (36) was true, the coupled equations (7) and (9) would be reduced to one equation in  $\rho$ . Therefore, and because  $\rho$  is real valued, the Schrödinger equation would be equivalent to an equation with a real valued unknown function. This is not true in general. It is only when the set  $(\rho, \varepsilon)$  is chosen that  $\mathbf{J}_\rho$  becomes a functional of  $(\rho, \varepsilon)$  and then (36) must be rewritten

$$\frac{\partial}{\partial t}\mathbf{J}_\rho = \mathbf{G}(\rho, \varepsilon) = -\frac{\partial}{\partial t}\left[\frac{1}{m}\rho \int_0^t \left(\frac{\varepsilon(t')}{\rho(t')}\right) dt'\right] \tag{37}$$

for TI one-body potentials.

For TD one-body potentials, all the preceding arguments are true. We have only to transform the results in §§ 2 and 3 to take into account a TD term. Short calculations for a one-body potential, with  $\hat{H}$  transformed in  $\hat{H}(t) = \hat{H} + \hat{V}_p(\mathbf{r}, t)$  and  $\hat{V}_p(\mathbf{r}, t)$  the TD term, lead to

$$\mathbf{J}_\rho = -\frac{\rho}{m}\nabla \int_0^t \left(\frac{\varepsilon(t')}{\rho(t')} + V_p(t')\right) dt' \tag{38}$$

$$\mathbf{J}_\varepsilon = \frac{\mathbf{J}_\rho \cdot \varepsilon}{\rho} + \mathbf{J}_\rho \cdot \mathbf{V}_p - \frac{\hbar^2}{4m}\rho\nabla\left(\frac{1}{\rho}\nabla \cdot \mathbf{J}_\rho\right) \tag{39}$$

for the functionals. The conservation equation (7) is unchanged for the  $V_p(\mathbf{r}, t)$  considered and the conservation equation (19) becomes

$$\frac{\partial}{\partial t}\varepsilon + \nabla \cdot \mathbf{J}_\varepsilon = -\frac{\partial}{\partial t}(V_p \cdot \rho). \tag{40}$$

As in the TI case,  $\mathbf{J}_\rho$  becomes a density functional only when the chosen set is  $(\rho, \varepsilon)$ . The TD term  $\hat{V}_p(\mathbf{r}, t)$  can be an external perturbation term or the TD part of an effective one-body potential coming from a many-body potential. In this case, the set  $(\rho, \varepsilon)$  can only be used if a development of  $V_p(\mathbf{r}, t)$  on  $(\rho, \varepsilon)$  exists.

### 5. Conclusion

There are at least two methods for solving a Schrödinger equation: spectral decomposition and polar decomposition of the wavefunction. The second method gives a choice between four sets of unknown real valued functions defined on  $C_S \times R$ :  $(\phi, \theta), (\rho, \mathbf{V})$ ,

$(\rho, \mathbf{J}_\rho)$  and  $(\rho, \varepsilon)$ . In the hydrodynamic approach  $(\rho, \mathbf{V})$  or  $(\rho, \mathbf{J}_\rho)$  are often used. However, we have shown the possibility of choosing also  $(\rho, \varepsilon)$  because at the NR level  $\mathbf{J}_\rho$  and  $\mathbf{J}_\varepsilon$  are each exact functionals of  $(\rho, \varepsilon)$ . This proves for TD one-body Hamiltonians, like those studied by Runge and Gross, that  $\mathbf{J}_\rho$  is not only a  $\rho$  functional.

Work is now in progress to use the  $\mathbf{J}_\rho$  and  $\mathbf{J}_\varepsilon$  decomposition on  $(\rho, \varepsilon)$  to calculate the response coefficients of a quantum system composed of an intermediate number of particles ( $2 \ll n_1 + n_2 \ll 10^{23}$ ) i.e. to reach the reduced level with  $\rho$  and  $\varepsilon$  as unknowns defined on  $R^4$ .

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