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Matthias Schmidt

Citation: The Journal of Chemical Physics **143**, 174108 (2015); doi: 10.1063/1.4934881
View online: http://dx.doi.org/10.1063/1.4934881
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/143/17?ver=pdfcov
Published by the AIP Publishing

Quantum power functional theory for many-body dynamics

Matthias Schmidt[a)]
Theoretische Physik II, Physikalisches Institut, Universität Bayreuth, D-95440 Bayreuth, Germany

(Received 18 June 2015; accepted 19 October 2015; published online 4 November 2015)

We construct a one-body variational theory for the time evolution of nonrelativistic quantum many-body systems. The position- and time-dependent one-body density, particle current, and time derivative of the current act as three variational fields. The generating (power rate) functional is minimized by the true current time derivative. The corresponding Euler-Lagrange equation, together with the continuity equation for the density, forms a closed set of one-body equations of motion. Space- and time-nonlocal one-body forces are generated by the superadiabatic contribution to the functional. The theory applies to many-electron systems. © *2015 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4934881]

I. INTRODUCTION

In both classical and quantum systems, it is the coupling of a large number of degrees of freedom that generates the wealth of equilibrium and dynamical phenomena of condensed matter. Successful microscopic theoretical descriptions of this fundamental physical mechanism are often based on simple model Hamiltonians and corresponding equations of motion that allow to simplify the complexity of a real system to its bare bones, while retaining the coupled, correlated nature of the many-body problem. While the availability of modern computers and advanced numerical techniques often allows to simulate the many-body problem directly, often an appropriate reformulation can provide deeper insights.

For equilibrium properties, the reformulation in a one-body variational language, which allows to reduce the complexity of high-dimensional Hilbert space (in the quantum case) or phase space distributions (for classical systems) to one-body fields, which depend only on a single space (and time) coordinate, has proved to be particularly successful. The framework of density functional theory (DFT) allowed to put earlier approximations for electronic structure, such as the Thomas-Fermi and Hartree-Fock theories, on a rigorous footing, via the Hohenberg-Kohn (HK) theorem,[1] which establishes the ground-state energy as a unique functional of the one-body density distribution $n(\mathbf{r})$, where $\mathbf{r}$ indicates position. Only one year after HK's groundbreaking paper, Mermin[2] generalized their theorem to non-zero temperature, thus introducing entropic contributions to what becomes the grand potential functional. The *classical* version of finite temperature DFT[3–5] has enabled us to systematically treat, on a unified footing, a broad range of equilibrium phenomena in liquids, both in bulk (freezing) and at surfaces (wetting) and in confinement (capillary condensation).

Variational treatments of nonequilibrium phenomena, however, whether in steady state or with full time-dependence, are currently primarily based on adiabatic extensions of the corresponding equilibrium framework. For electronic structure, the Runge-Gross[6,7] procedure provides a stationarity condition on an action functional, which is unknown, such that one typically has to resort to adiabatic approximations. The dynamical density functional theory (DDFT)[4,5,8] for classical systems, as first suggested by Evans in 1979, is derived from approximating the true nonequilibrium two-body density correlator with a fictitious equilibrium distribution, and then using an equilibrium sum rule in order to introduce the (equilibrium) free energy functional into the dynamical theory,[9] hence neglecting any effects beyond the adiabatic description.

Recent progress allowed to systematically trace the superadiabatic forces in classical Brownian systems as originating from functional differentiation of an excess (over ideal gas) free power dissipation functional.[10,11] The importance of these forces was demonstrated by explicit many-body simulations.[12] In nonequilibrium, the free power functional plays a role analogous to that of the free energy functional in equilibrium. This (power functional) theory addresses many-body overdamped Brownian motion, as described by the Smoluchowski equation, i.e., the Fokker-Planck equation for the (classical) probability distribution in configuration space. Although the Smoluchowski equation is entirely real, due to its drift-diffusion form, it shares many structural similarities with the Schrödinger equation of nonrelativistic quantum mechanics. However, besides the conceptual differences between quantum and classical motions, there is also a number of formal distinctions, due to the wave function being complex, the sandwich form of quantum mechanical expectation values, and the differences of inertial and overdamped dynamics.

In the present paper, we construct a quantum power functional theory by systematically addressing all the above differences. The central generating quantum (power rate) functional G_t^{int} is an intrinsic object, in that it depends solely on the interparticle interactions, but not on the external fields. The functional dependence is nonlocal in space and time via three one-body fields, i.e., the density, the current, and the time derivative of the current. We prove an exact minimization principle with respect to the time derivative of the current, which determines the physical dynamics. An explicit (formal) expression for the corresponding quantum (power rate) functional is given and its structure is discussed.

a)Electronic address: Matthias.Schmidt@uni-bayreuth.de

II. VARIATIONAL THEORY

The Schrödinger equation in position representation is

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r}^N,t) = \hat{H}\Psi(\mathbf{r}^N,t), \tag{1}$$

where i is the imaginary unit, $\hbar$ is the reduced Planck constant, t indicates time, $\mathbf{r}^N \equiv \{\mathbf{r}_1 \ldots \mathbf{r}_N\}$ denotes the positions of the N quantum particles, and $\Psi(\mathbf{r}^N,t)$ is the quantum mechanical wave function. We consider many-body Hamiltonians of the form

$$\hat{H} = \sum_i \frac{\hat{\mathbf{p}}_i^2}{2m} + u(\mathbf{r}^N) + \sum_i v^{\mathrm{ext}}(\mathbf{r}_i,t), \tag{2}$$

where the sums run over all N particles, m indicates the particle mass, $u(\mathbf{r}^N)$ is the (intrinsic) interparticle interaction potential (i.e., the Coulomb potential in case of electrons), and $v^{\mathrm{ext}}(\mathbf{r},t)$ is a position- and time-dependent external one-body potential energy. The (kinematic) momentum operator of quantum particle i is given in position representation as

$$\hat{\mathbf{p}}_i = -\mathrm{i}\hbar\nabla_i - q\mathbf{A}(\mathbf{r}_i,t), \tag{3}$$

where ∇_i indicates the derivative with respect to $\mathbf{r}_i$, q is the electrical particle charge, and $\mathbf{A}(\mathbf{r},t)$ is the position- and time-dependent magnetic vector potentials.[13] Applying the general Heisenberg equation of motion for an operator $\hat{O}$,

$$\frac{d\hat{O}}{dt} = \frac{\mathrm{i}}{\hbar}[\hat{H},\hat{O}] + \frac{\partial\hat{O}}{\partial t}, \tag{4}$$

to the ith position and momentum operator yields

$$\frac{d\mathbf{r}_i}{dt} = \frac{\hat{\mathbf{p}}_i}{m}, \tag{5}$$

$$\frac{d\hat{\mathbf{p}}_i}{dt} = \hat{\mathbf{f}}_i, \tag{6}$$

where $\hat{\mathbf{f}}_i$ is the force operator of particle i, obtained as

$$\hat{\mathbf{f}}_i = -(\nabla_i u) - (\nabla_i v_i^{\mathrm{ext}}) - q\dot{\mathbf{A}}_i + \frac{q}{2m}(\hat{\mathbf{p}}_i\times\mathbf{B}_i - \mathbf{B}_i\times\hat{\mathbf{p}}_i), \tag{7}$$

where $v_i^{\mathrm{ext}} = v^{\mathrm{ext}}(\mathbf{r}_i,t)$, the magnetic field acting on particle i is given by the multiplication operator $\mathbf{B}_i \equiv \mathbf{B}(\mathbf{r}_i,t)$, obtained from the vector potential via $\mathbf{B}(\mathbf{r},t) = \nabla\times\mathbf{A}(\mathbf{r},t)$, which arises from the fact that $[\hat{p}_i^\alpha,\hat{p}_i^\beta] = \mathrm{i}q\hbar\sum_\gamma\epsilon_{\alpha\beta\gamma}B_i^\gamma$, where Greek indices indicate Cartesian vector components and $\epsilon_{\alpha\beta\gamma}$ is the Levi-Civita symbol; furthermore, $\dot{\mathbf{A}}_i \equiv \partial\mathbf{A}(\mathbf{r}_i,t)/\partial t$. Eq. (7) represents the sum of all forces that act on quantum particle i, with contributions due to the interparticle interaction potential, the external potential, and the Lorentz force. Both vector fields $-(\nabla_i u)$ and $-(\nabla_i v^{\mathrm{ext}})$ are multiplication operators, such that the derivative only acts inside of the brackets.

We turn to a description on the level of space- and time-dependent one-body fields. Consider first the density operator $\hat{n}_i \equiv \delta_i$ of quantum particle i, where $\delta_i \equiv \delta(\mathbf{r}-\mathbf{r}_i)$ indicates the three-dimensional Dirac distribution. Using (4) yields an equation of motion of continuity form

$$\frac{d\hat{n}_i}{dt} = -\nabla\cdot\hat{\mathbf{J}}_i, \tag{8}$$

where ∇ indicates the derivative with respect to $\mathbf{r}$ and the current operator of quantum particle i is given by

$$\hat{\mathbf{J}}_i(\mathbf{r},t) = \frac{\hat{\mathbf{p}}_i\delta_i + \delta_i\hat{\mathbf{p}}_i}{2m}. \tag{9}$$

Differentiating in time once more yields, via (4),

$$m\frac{d\hat{\mathbf{J}}_i}{dt} = \frac{\hat{\mathbf{f}}_i\delta_i + \delta_i\hat{\mathbf{f}}_i}{2} + \nabla\cdot\hat{\boldsymbol{\tau}}_i + \frac{\hbar^2}{4m}\Delta\nabla\hat{n}_i, \tag{10}$$

where $\hat{\mathbf{f}}_i$ is defined by (7) and the one-body momentum current (or local kinematic stress tensor) of particle i is given by

$$\hat{\boldsymbol{\tau}}_i(\mathbf{r},t) = -\frac{\hat{\mathbf{p}}_i\delta_i\hat{\mathbf{p}}_i + (\hat{\mathbf{p}}_i\delta_i\hat{\mathbf{p}}_i)^{\mathsf{T}}}{2m}. \tag{11}$$

Here, all pairs of vectors form dyadic products, and the superscript T denotes the transpose of the Cartesian components of a three-dimensional matrix. The second and third term in (10) (where $\Delta = \nabla\cdot\nabla$) describe the transport effects that are due to the one-body description; these effects are absent in the "bare" motion (6) and (7).

We build expectation values via the standard procedure, e.g., for the particle-labelled (Schrödinger) density operator $\hat{n}_i$, the corresponding average is

$$n(\mathbf{r},t) = \Big\langle\sum_i\hat{n}_i\Big\rangle \equiv \int d\mathbf{r}^N\Psi^*(\mathbf{r}^N,t)\sum_i\hat{n}_i\Psi(\mathbf{r}^N,t), \tag{12}$$

where the asterisk denotes complex conjugation and $\Psi(\mathbf{r}^N,t)$ satisfies (1) and is normalized at all times, $\int d\mathbf{r}^N\Psi^*\Psi = 1$. Corresponding expressions for the one-body current $\mathbf{J}(\mathbf{r},t)$ and momentum current tensor $\boldsymbol{\tau}(\mathbf{r},t)$ are obtained by using $\hat{\mathbf{J}}_i$ and $\hat{\boldsymbol{\tau}}_i$, respectively, instead of $\hat{n}_i$ in (12).

Building the expectation value of (8) and integrating in time yields

$$n(\mathbf{r},t) = n(\mathbf{r},t_0) - \int_{t_0}^t dt'\nabla\cdot\mathbf{J}(\mathbf{r},t'), \tag{13}$$

$$\mathbf{J}(\mathbf{r},t) = \mathbf{J}(\mathbf{r},t_0) + \int_{t_0}^t dt'\dot{\mathbf{J}}(\mathbf{r},t'), \tag{14}$$

where t_0 is an initial time, at which the state of the system is assumed to be known. The symmetry of the many-body wave function at this initial time encodes the particle statistics. Eqs. (13) and (14) allow to determine n and $\mathbf{J}$, provided that the time derivative of the current, $\dot{\mathbf{J}}$, is known. One way of obtaining $\dot{\mathbf{J}}$ is to build the expectation value of (10) and summing over i, which yields

$$m\dot{\mathbf{J}}(\mathbf{r},t) = \mathbf{f}^{\mathrm{int}} - (q\dot{\mathbf{A}} + \nabla v^{\mathrm{ext}})n + q\mathbf{J}\times\mathbf{B} + \nabla\cdot\boldsymbol{\tau} + \frac{\hbar^2}{4m}\Delta\nabla n, \tag{15}$$

where the interparticle interactions generate the intrinsic force density field,

$$\mathbf{f}^{\mathrm{int}}(\mathbf{r},t) = -\Big\langle\sum_i(\nabla_i u)\delta_i\Big\rangle. \tag{16}$$

The second and third terms in (15) represent the external forces; the fourth and fifth terms constitute transport contributions.

In the following, we construct an alternative to (15) and (16), by expressing the physical dynamics via a variational approach. We start on the many-body level and introduce a set of (complex) acceleration fields $\mathbf{a}^N \equiv \{\mathbf{a}_1(\mathbf{r}^N,t)\ldots\mathbf{a}_N(\mathbf{r}^N,t)\}$, which act as variational variables. In the spirit of Gauss' principle of least constraint for classical systems, as formalized independently by Appell and Gibbs,[14] we define an instantaneous functional of the acceleration fields as

$$\mathcal{G}_t = \int d\mathbf{r}^N \sum_i \frac{|(\hat{\mathbf{f}}_i - m\mathbf{a}_i)\Psi|^2}{2m} - \int d\mathbf{r}\frac{m}{2\langle\hat{n}\rangle}\left\langle\frac{d\hat{\mathbf{J}}}{dt}\right\rangle^2, \tag{17}$$

where $\hat{n} = \sum_i \hat{n}_i$ and the total time derivative of $\hat{\mathbf{J}}$ is given via (10) summed over all i. Note that the first term on the right-hand side of (17) possesses the structure $\int d\mathbf{r}^N|\hat{O}\Psi|^2 \equiv \langle\hat{O}^\dagger\hat{O}\rangle$, where † indicates the Hermitian adjoint.

Minimizing (17) with respect to $\mathbf{a}^N$ at fixed time t implies that

$$\frac{\delta\mathcal{G}_t}{\delta\mathbf{a}_i(\mathbf{r}^N,t)} = 0, \tag{18}$$

for all $i = 1\ldots N$, and that the trial fields satisfy

$$m\mathbf{a}_i(\mathbf{r}^N,t)\Psi(\mathbf{r}^N,t) = \hat{\mathbf{f}}_i\Psi(\mathbf{r}^N,t), \tag{19}$$

at time t. The equality in (18) and (19) is attained for the specific $\mathbf{a}^N$ at the minimum. Correspondingly, $\mathbf{p}^N$ and $\mathbf{r}^N$, and hence $\boldsymbol{\tau}^N$ via (11), are then determined by integrating (5) and (6).

As a further central property, $\mathcal{G}_t$ acts as a generator for the one-body field of interest, via functional differentiation,

$$\frac{\delta\mathcal{G}_t}{\delta q\dot{\mathbf{A}}(\mathbf{r},t)} = \dot{\mathbf{J}}(\mathbf{r},t). \tag{20}$$

In order to connect the many-body description with the one-body level, we introduce a constraint on the acceleration fields $\mathbf{a}^N$ via

$$\dot{\mathbf{J}}(\mathbf{r},t) = \Big\langle\sum_i\Big(\frac{\mathbf{a}_i+\mathbf{a}_i^*}{2}\delta_i + \frac{\nabla\cdot\hat{\boldsymbol{\tau}}_i}{m} + \frac{\hbar^2}{4m^2}\Delta\nabla\hat{n}_i\Big)\Big\rangle, \tag{21}$$

where $\dot{\mathbf{J}}(\mathbf{r},t)$ is regarded as a prescribed "target" one-body function. Hence in general, there will be many choices of $\mathbf{a}^N$ that are compatible with a given $\dot{\mathbf{J}}$; we indicate this relationship (21) by $\mathbf{a}^N \to \dot{\mathbf{J}}$.

Performing a constrained search[15,16] for the minimum,

$$G_t[n,\mathbf{J},\dot{\mathbf{J}}] = \min_{\mathbf{a}^N\to n,\mathbf{J},\dot{\mathbf{J}}}\mathcal{G}_t, \tag{22}$$

establishes G_t as a functional of the three one-body fields $n,\mathbf{J}$, and $\dot{\mathbf{J}}$. If $\mathbf{J}$ and n possess those values that correspond to the physical dynamics, then G_t is minimized by the true $\dot{\mathbf{J}}(\mathbf{r},t)$, and hence possesses vanishing (functional) derivative,

$$\frac{\delta G_t[n,\mathbf{J},\dot{\mathbf{J}}]}{\delta\dot{\mathbf{J}}(\mathbf{r},t)} = 0. \tag{23}$$

We proceed by splitting total power rate (22) into intrinsic and external contributions,

$$G_t = G_t^{\rm int} - \int d\mathbf{r}\,\dot{\mathbf{J}}\cdot\left(\frac{q\mathbf{J}\times\mathbf{B}}{n} - q\dot{\mathbf{A}} - \nabla v^{\rm ext}\right), \tag{24}$$

where the intrinsic functional $G_t^{\rm int}[n,\mathbf{J},\dot{\mathbf{J}}]$ is independent of the external fields. Due to (20), the splitting constitutes a Legendre transform from G_t to $G_t^{\rm int}$. Inserting (24) into the one-body variational equation (23) yields an equality of intrinsic and external contributions,

$$\frac{\delta G_t^{\rm int}}{\delta\dot{\mathbf{J}}} = \frac{q\mathbf{J}\times\mathbf{B}}{n} - q\dot{\mathbf{A}} - \nabla v^{\rm ext}, \tag{25}$$

where the left hand side contains the interparticle interactions, as well as acceleration and transport effects.

We further decompose the intrinsic power rate functional $G_t^{\rm int}$ into ideal (i.e., noninteracting, $u = 0$, single-particle motion) and excess (above ideal, exchange and correlation) contributions according to

$$G_t^{\rm int} = G_t^{\rm id} + G_t^{\rm exc}, \tag{26}$$

where for ideal motion, the intrinsic contribution is

$$G_t^{\rm id}[n,\mathbf{J},\dot{\mathbf{J}}] = \int d\mathbf{r}\,\frac{\dot{\mathbf{J}}}{n}\cdot\left(\frac{m\dot{\mathbf{J}}}{2} - \nabla\cdot\boldsymbol{\tau}^{\rm id} - \frac{\hbar^2}{4m}\nabla\Delta n\right), \tag{27}$$

with the ideal momentum current possessing the factorized dyadic form

$$\boldsymbol{\tau}^{\rm id}(\mathbf{r},t) = -m\frac{\mathbf{J}\mathbf{J}}{n} - \frac{\hbar^2}{4m}\frac{(\nabla n)(\nabla n)}{n}. \tag{28}$$

The excess (over ideal) contribution $G_t^{\rm exc}$ in (26) contains the effects of the intrinsic interactions u. Inserting (26) and (27) into (25) yields an exact relation for the time derivative of the current

$$\begin{aligned} m\dot{\mathbf{J}} = &-n\frac{\delta G_t^{\rm exc}}{\delta\dot{\mathbf{J}}} + \nabla\cdot\boldsymbol{\tau}^{\rm id} + \frac{\hbar^2}{4m}\nabla\Delta n \\ &+ q\mathbf{J}\times\mathbf{B} - (q\dot{\mathbf{A}} + \nabla v^{\rm ext})n, \end{aligned} \tag{29}$$

which together with continuity equations (13) and (14) forms a closed set of equations of motion for the one-body fields. Note that the splittings (24) and (26) define $G_t^{\rm int}$ and $G_t^{\rm exc}$, respectively; hence, these relations do not constitute assumptions. In the non-interacting case, $G_t^{\rm exc} = 0$ and (29) reduces to the exact equation of motion for the ideal system. In the interacting case, the many-body problem is now encapsulated in the complexity of the dependence of $G_t^{\rm exc}[n,\mathbf{J},\dot{\mathbf{J}}]$ on its arguments. Comparing Eqs. (15) and (29) yields the identification

$$\frac{\delta G_t^{\rm exc}}{\delta\dot{\mathbf{J}}} = \frac{\mathbf{f}^{\rm int} + \nabla\cdot(\boldsymbol{\tau} - \boldsymbol{\tau}^{\rm id})}{n}, \tag{30}$$

where the functional derivative is evaluated at the minimum of the functional, i.e., for the true value of $\dot{\mathbf{J}}$.

The (approximate) description of the effects of interparticle interactions can now be formulated using appropriate model forms for the excess power rate functional $G_t^{\rm exc}$. If we assume a splitting into a sum of adiabatic and superadiabatic contributions, then

$$G_t^{\rm exc} = \int d\mathbf{r}\,\dot{\mathbf{J}}\cdot\nabla\frac{\delta E[n]}{\delta n} + G_t^{\rm sup}, \tag{31}$$

where the first (adiabatic) term originates from the second time derivative of the (ground state) intrinsic potential energy functional $E[n]$,

$$\frac{d^2E[n]}{dt^2} = \int d\mathbf{r}\,\dot{\mathbf{J}}\cdot\nabla\frac{\delta E}{\delta n} + \int d\mathbf{r}d\mathbf{r}'\,\mathbf{J}'\mathbf{J}:\nabla\nabla'\frac{\delta^2E}{\delta n\delta n'}, \tag{32}$$

where $\mathbf{J}' \equiv \mathbf{J}(\mathbf{r}',t)$, $n' = n(\mathbf{r}',t)$, and the colon indicates a double tensor contraction. Hence, we obtain the Euler-Lagrange equation (29) in the more explicit form

$$m\dot{\mathbf{J}} = -n\frac{\delta G_t^{\mathrm{sup}}}{\delta \dot{\mathbf{J}}} - n\nabla\frac{\delta E}{\delta n} + \nabla\cdot\boldsymbol{\tau}^{\mathrm{id}} + \frac{\hbar^2}{4m}\nabla\Delta n + q\mathbf{J}\times\mathbf{B} - (q\dot{\mathbf{A}} + \nabla v^{\mathrm{ext}})n, \tag{33}$$

where the superadiabatic power rate $G_t^{\mathrm{sup}}[n,\mathbf{J},\dot{\mathbf{J}}]$ (as defined via Eq. (31)) depends in general nonlocally in space and time on its arguments and describes superadiabatic contributions to the dynamics. Clearly, the description of the adiabatic reference state could be extended by using a current-density functional, instead of $E[n]$. Furthermore, it is not guaranteed that the ground state of the fictitious adiabatic system constitutes a good reference, see, e.g., Ref. 12 for a corresponding classical study.

III. CONCLUSIONS

The present procedure can readily be applied to the Kohn-Sham framework of representing the total density by superposition of noninteracting single-particle orbitals. The same superposition applies to the current and its time derivative, and in turn, the forces obtained from the power functional governs the dynamics of the single-particle orbitals.

Constructing usable approximations for the superadiabatic contribution to the power rate functional, G_t^{sup} constitutes a necessary research task for the future. Similar to the classical case,[10] a low-order functional expansion could constitute a suitable model, where the convolution kernel M depends in general functionally on $\mathbf{J}$ and n. The resulting superadiabatic force is then given by

$$\frac{\delta G_t^{\mathrm{sup}}}{\delta \dot{\mathbf{J}}(\mathbf{r},t)} = \int_{t_0}^{t} dt' \int d\mathbf{r}'\, \mathsf{M}(\mathbf{r},t;\mathbf{r}',t')\cdot\dot{\mathbf{J}}(\mathbf{r}',t'), \tag{34}$$

which can be further simplified by assuming that M is a delta function in space and/or time. Generalizing the quantum version[17] of the Ornstein-Zernike equation to the dynamical case, as has been done for Brownian systems,[11] constitutes a further exciting prospect.

ACKNOWLEDGMENTS

D. de las Heras, Th. M. Fischer, and I. Bauer are acknowledged for useful discussions. This work would not have come to fruition without the inspiration and encouragement provided by J. M. Brader.

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