PHYSICAL REVIEW A VOLUME 31, NUMBER 3 MARCH 1985

Hohenberg-Kohn theorem for time-dependent ensembles

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(Received 20 August 1984)

It is proven that the Runge-Gross version of the Hohenberg-Kohn theorem is valid for arbitrary time-dependent ensembles.

In a very recent Letter,[1] Runge and Gross (RG) have developed a density-functional formalism comparable to the Hohenberg-Kohn-Sham[2,3] theory of the ground state for time-dependent (TD) systems described by the Schrödinger equation, i.e., for arbitrary TD systems of pure states.

In this Brief Report, we would like to prove that the RG version of the Hohenberg-Kohn (HK) theorem holds also for arbitrary TD ensembles. The proof is very simple and similar to RG's mentioned above. Nevertheless, it greatly enlarges the realm of RG theorem (the RG version of the HK theorem).

The Hamiltonian of the system is

$$\hat{H}(t)=\hat{T}+\hat{V}(t)+\hat{W}\ , \tag{1}$$

in which a TD, local, and spin-independent single-particle potential

$$\hat{V}(t)=\sum_s\int d^3r\hat{\psi}_s^\dagger(\vec{r})v(\vec{r},t)\hat{\psi}_s(\vec{r})$$

is assumed, and added to the kinetic energy and some spin-independent particle-particle interaction

$$\hat{W}=\tfrac{1}{2}\sum_s\sum_{s'}\int d^3r\int d^3r'\hat{\psi}_s^\dagger(\vec{r})\hat{\psi}_{s'}^\dagger(\vec{r}')w(\vec{r},\vec{r}')\times\hat{\psi}_{s'}(\vec{r}')\hat{\psi}_s(\vec{r})\ .$$

Let $v(\vec{r},t)$ and $v'(\vec{r},t)$ be two potentials, which belong to two different classes [i.e., two inequivalent elements: $v(\vec{r},t)-v'(\vec{r},t)\neq c(t)$] and can be expanded into a Taylor series around an initial time t_0 when $\hat{\rho}(t_0)=\hat{\rho}'(t_0)$, where $\hat{\rho}$ and $\hat{\rho}'$ are the density operators corresponding to $\hat{H}(t)$ and $\hat{H}'(t)=\hat{T}+\hat{V}'(t)+\hat{W}$, respectively. As pointed out by RG,[1] there must exist some minimal non-negative integer k such that

$$\nabla\frac{\partial^k}{\partial t^k}[v(\vec{r},t)-v'(\vec{r},t)]\Big|_{t=t_0}\neq 0\ . \tag{2}$$

The measured value and its derivative of any observable of the ensemble is given by

$$\bar{O}(t)=\mathrm{tr}[\hat{\rho}(t)\hat{O}(t)] \tag{3}$$

and

$$i\frac{d\bar{O}(t)}{dt}=\mathrm{tr}\left(\hat{\rho}(t)i\frac{\partial\hat{O}(t)}{\partial t}\right)-\mathrm{tr}\{[\hat{\rho}(t),\hat{H}(t)]\hat{O}(t)\}$$
$$=\mathrm{tr}\left(\hat{\rho}(t)i\frac{\partial\hat{O}(t)}{\partial t}\right)+\mathrm{tr}\{\hat{\rho}(t)[\hat{O}(t),\hat{H}(t)]\} \tag{4}$$

according to Liouville's theorem

$$i\frac{\partial\hat{\rho}(t)}{\partial t}=[\hat{H}(t),\hat{\rho}(t)] \tag{5}$$

and the cyclic property for the trace. Applying Eqs. (3)–(5) repeatedly to the current operator

$$\hat{j}(r)=\frac{1}{2i}(\nabla'-\nabla)\hat{\psi}^\dagger(x')\hat{\psi}(x)|_{x'=x}\ ,$$

one has

$$i\frac{\partial\vec{j}(\vec{r},t)}{\partial t}=\mathrm{tr}\hat{\rho}(t)[\hat{j},\hat{H}(t)]\ , \tag{6}$$

$$\left(i\frac{\partial}{\partial t}\right)^2\vec{j}(\vec{r},t)=\mathrm{tr}\hat{\rho}(t)\left[\hat{j},i\frac{\partial\hat{H}(t)}{\partial t}\right]+\mathrm{tr}\hat{\rho}(t)[[\hat{j},\hat{H}(t)],\hat{H}(t)]\ , \tag{6$'$}$$

and generally

$$\left(i\frac{\partial}{\partial t}\right)^{k+1}\vec{j}(\vec{r},t)=\mathrm{tr}\hat{\rho}(t)\left[\hat{j},\left(i\frac{\partial}{\partial t}\right)^k\hat{H}(t)\right]+\cdots\ , \tag{6$''$}$$

where $\cdots$ represents the remaining terms. One can easily prove that except for the direct kth derivative term the contribution of the remaining terms of the right-hand side (RHS) of (6$''$) is exactly eliminateable at moment t_0, by using Eq. (2) and the cyclic property:

$$[[\hat{A},\hat{B}]\hat{C}]+[[\hat{B},C],\hat{A}]+[[\hat{C},\hat{A}],\hat{B}]=0\ .$$

Thus, we obtain the same results for arbitrary ensembles as RG have given for pure states:

$$\left(i\frac{\partial}{\partial t}\right)^{k+1}[\vec{j}(\vec{r},t)-\vec{j}'(\vec{r},t)]\Big|_{t=t_0}=in(\vec{r},t_0)\nabla\left[\left(i\frac{\partial}{\partial t}\right)^k[v(\vec{r},t)-v'(\vec{r},t)]\Big|_{t=t_0}\right]\neq 0 \tag{7}$$

and

$$\frac{\partial^{k+2}}{\partial t^{k+2}}[n(\vec{r},t)-n'(\vec{r},t)]\Big|_{t=t_0}=-\mathrm{div}\,n(\vec{r},t_0)\nabla\left(\frac{\partial^k}{\partial t^k}[v(\vec{r},t)-v'(\vec{r},t)]\Big|_{t=t_0}\right) \tag{8}$$

by using the continuity equation

$$\frac{\partial}{\partial t}n(\vec{r},t)+\mathrm{div}\,\vec{j}(\vec{r},t)=0\ .$$

The remaining algebraic proof by *reductio ad absurdum* to show the rhs of (8) cannot vanish if (2) holds, is just the same as what RG have done for their theorem 1, and we will not repeat it here. Taking a three-component density functional

$$\vec{P}[n](\vec{r},t) = -i\,\mathrm{tr}\hat{\tilde{\rho}}(t)[\hat{j}(\vec{r}),\hat{\tilde{H}}(t)] \ ,$$

where $\hat{\tilde{H}}(t)=\hat{H}(t)-c(t)$, and $\hat{\tilde{\rho}}[n](t)$ is defined as the density operator obtained for the choice of $\tilde{v}(r,t)$, $\hat{\tilde{\rho}}[n](t)=e^{i\alpha(t)}\hat{\rho}e^{-i\alpha(t)}$, $\dot{\alpha}=c(t)$, one can easily prove that also RG's theorem 2 holds for ensembles by using Eq. (6). In fact, $\tilde{v}(r,t)=v(r,t)-c(t)$ is a representative element of the potential class. In this element no additive TD function $c(t)$ can be separated. Since we have proved a one-to-one map between an ensemble v-representable density [i.e., the density that results from the solution of Eq. (5)] and potential $v(\vec{r},t)$ (up to an additive TD function) for a given initial state of the system, i.e., an uniqueness theorem, then the density operator of the ensemble itself is a density-functional $\hat{\rho}=\hat{\rho}[n](t)$.

Twenty years have passed since the proof of the HK theorem, a foundation for density-functional theory for the nondegenerate ground state. Density-functional theory has succeeded remarkably in many fields. Nevertheless, to further develop its basic theory is a difficult task, and many open problems still remain to be resolved. Yet people have enlarged the realm of the original HK theorem to degenerate ground states,[4] thermodynamic equilibriuim systems,[5] and to arbitrary TD pure states,[1] as well as arbitrary TD ensembles described by Liouville's theorem in the RG version.

One of the authors (T.C.L.) would like to thank Professor W. Kohn for his excellent lectures given in Beijing during this visit and for helpful discussions which stimulated the author's interest in this field. Thanks are also due to Professor R. M. Dreizler, Dr. E. Runge, and Dr. E. K. U. Gross for their kind correspondence and for sending us their paper before publication.

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