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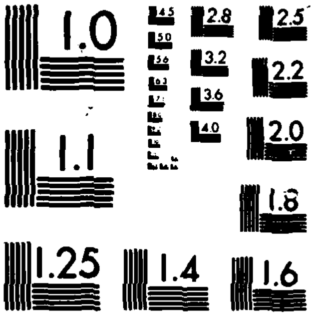

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TECHNICAL REPORT NO. 9

Density functional theory for excited states in a quasi local density approximation

by

W. Kohn

Department of Physics
University of California, Santa Barbara
Santa Barbara, CA 93106

Density functional theory has been an important method for studying the ground states for systems involving interacting electrons such as atoms, molecules, and solids. This paper helps to extend this theory to excited states.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The starting point of this paper is a recent extension by A. K. Theophilou of the Hohenberg-Kohn-Sham (HKS) density functional theory to ensembles of systems consisting of the M lowest eigenstates, equally weighted. As in the HKS theory the key quantities are the exchange correlation energy, $E_{xc}^{M}[n(r')]$ and potential $v_{xc}^{M}(r;[n(r')])$. The present paper provides

expressions for these quantities, valid for systems of slowly varying density. Even for such systems, however, there are essential non-local effects. Nevertheless both E_{xc}^{M} and v_{xc}^{M} can be calculated in terms of quantities characteristic of appropriate uniform thermal ensembles. This theory is the analog of the ground state local density approximation and allows calculation of excited state energies and densities.

Density Functional Theory for Excited States in a Quasi Local Density Approximation

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ABSTRACT

The starting point of this paper is a recent extension by A.K. Theophilou of the Hohenberg-Kohn-Sham (HKS) density functional theory to ensembles of systems consisting of the M lowest eigenstates, equally weighted. As in the HKS theory the key quantities are the exchange correlation energy, $E_{xc}^{M}[n(r')]$ and potential $v_{xc}^{M}(r;[n(r')])$. The present paper provides expressions for these quantities, valid for systems of slowly varying density. Even for such systems, however, there are essential non-local effects. Nevertheless both E_{xc}^{M} and v_{xc}^{M} can be calculated in terms of quantities characteristic of appropriate uniform thermal ensembles. This theory is the analog of the ground state local density approximation and allows calculation of excited state energies and densities.

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The ground state density functional theory of Hohenberg, Kohn and Sham (HKS)[1,2] was formally extended by Theophilou[3] to the mean energy, E^M, and mean density, $n(r)$, of an ensemble consisting of the lowest M states equally weighted by the factor 1/M. (We shall call such an ensemble an equi-ensemble.) This theory allows, in principle, the calculation of individual excited state energies and densities, E_m and $n_m(r)$. In analogy with the HKS theory, the essential required quantities are the exchange-correlation energy and potential, $E^M_{xc}[n(r')]$ and $v^M_{xc}(r,[n(r')])$, both functionals of the ensemble density $n(r')$.

The practical usefulness of the HKS ground state theory has been largely due to the simplicity and surprising accuracy of the so-called local density approximation (LDA),

$$\left.\begin{aligned} E_{xc}[n(r')] &= \int e_{xc}(n(r'))\,dr' && (1) \\ v_{xc}(r) &= \frac{d}{dn}\Big(e_{xc}(n)\Big)_{n=n(r)} && (2) \end{aligned}\right\}\ \text{LDA}$$

where $e_{xc}(n)$ is the exchange-correlation energy per unit volume of a uniform electron gas of density n in its ground state. The present paper reports briefly a generalization of the LDA to the equi-ensemble. A complete manuscript has been submitted to Physical Review A.

We remark first of all that expressions for E^M_{xc} and v^M_{xc} analogous to (1) and (2) do not exist. The reason is that, for given M, the contribution of a volume element dr to E^M_{xc}

depends strongly not only on the local density, ~~n (r),~~ but on the density, n(r'), everywhere else. Nevertheless, a quasi-LDA *is* possible for the equi-ensemble. This approximation is the more accurate the larger the number of particles, N, and the smoother the density n(r). The derivation proceeds via the thermodynamic equivalence of such a large and smooth equi-ensemble with a canonical ensemble of appropriate temperature θ. Temperature ensembles were first discussed by Mermin,[4)] and local density approximations for E^{θ}_{xc} and v^{θ}_{xc}, quite analogous to (1) and (2) *do* exist.[2)] However the temperature θ, of the canonical ensemble equivalent to the equi-ensemble of M states and average density n(r), depends both on M and on n(r') for *all* r'. Furthermore the temperature, θ_s, of the non-interacting (KS) canonical ensemble which is thermodynamically equivalent to the non-interacting (KS) ensemble of M states is different from θ.

Our final results are the following:

Consider a system of N electrons in a given external potential, v(r). The objective is to calculate the average density, n(r), and average energy, E^M, of the lowest M eigenstates[5)].

1. One requires the following thermodynamic functions,[6)] for homogeneous interacting and non-interacting electron gases, of the density n and temperature θ'. (The subscript s denotes non-interacting and the subscript 1 differentiation with respect to temperature.)
    a) The entropies per unit volume $\sigma^{\theta'}(n)$ and $\sigma^{\theta'}_s(n)$, and their temperature derivatives, $\sigma^{\theta'}_1(n)$ and $\sigma^{\theta'}_{s,1}(n)$.
    b) The exchange-correlation plus kinetic energy per unit volume $e^{\theta'}(n)$, and its temperature derivative $e^{\theta'}_1(n)$.
    c) The kinetic energy per unit volume of a non-interacting system, $t^{\theta'}_s(n)$, and its temperature derivative $t^{\theta'}_{s,1}(n)$.

2. Begin with an initial approximation to n(r). Determine the corresponding interacting temperature θ and non-interacting (KS) temperature θ_s by solving respectively the implicit equations

$$k \log M = \int \sigma^{\theta}(n(r))dr; \quad k \log M = \int \sigma_s^{\theta_s}(n(r))dr. \qquad (3)$$

3. Construct the effective one particle potential

$$v^M_{eff}(r) = v(r) + \int \frac{n(r')}{|r-r'|} dr' + v^M_{xc}(r;[n(r')]), \qquad (4)$$

where v^M_{xc} is given by the following expression:

$$v^M_{xc} = \frac{\partial}{\partial n}\left(e^{\theta}(n) - t_s^{\theta_s}(n)\right)_{n=n(r)} + \frac{\partial \theta}{\partial n(r)} \int e_1^{\theta}(n(r'))dr'$$

$$- \frac{\partial \theta_s}{\partial n(r)} \int t_{s,1}^{\theta_s}(n(r'))dr' \qquad (5)$$

where

$$\frac{\partial \theta}{\partial n(r)} = -\left(\frac{\partial \sigma^{\theta}(n)}{\partial n}\right)_{n=n(r)} \Big/ \int \sigma_1^{\theta}(n(r'))dr' \qquad (6)$$

and

$$\frac{\partial \theta_s}{\partial n(r)} = -\left(\frac{\partial \sigma_s^{\theta_s}(n)}{\partial n}\right)_{n=n(r)} \Big/ \int \sigma_{s,1}^{\theta}(n(r'))dr' . \qquad (7)$$

4. Solve the KS single-particle equations

$$(-\frac{1}{2}\nabla^2 + v_{eff}^{M}(r) - \varepsilon_i)\,\phi_i^{M}(r) = 0 \ . \qquad (10)$$

5. Construct the M lowest non-interacting N-particle wave-functions $\psi_{s,m}(m=1,\ldots M)$ and calculate their average density $n'(r)$[5].

6. If $n'(r) \equiv n(r)$, then the original $n(r)$ was self-consistent. If not, repeat steps 2-5, starting with a different initial density until self-consistency is achieved.

7. Now determine the average energy, E^M, of the equi-ensemble as follows. Let $E_{s,m}(m=1,\ldots M)$ be the energies of the M lowest KS states. Then

$$E^M = \text{Av}\ E_{s,m} - \frac{1}{2}\int \frac{n(r)n(r')}{|r-r'|}\,dr\,dr' - \int v_{xc}^{M}(r)n(r)dr$$

$$+ \int \{e^{\theta}(n(r)) - t_s^{\theta}(n(r))\}dr \ . \qquad (9)$$

By successive calculations for increasing M, starting with $M = 1$, the excited state energies E_m and densities $n_m(r)$ (averaged over multiplets) can be obtained. The quantitative accuracy of this quasi-LDA for systems in which N is not very large and/or n(r) is not slowly varying remains to be tested.

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References and Footnotes

1. P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).
2. W. Kohn and L. J. Sham, Phys. Rev. A 140, A1133 (1965).
3. A. K. Theophilou, J. Phys. C 12, 5419 (1979).
4. N. D. Mermin, Phys. Rev. 137, A1441 (1965).
5. When there is a degeneracy, all states of a multiplot are to be simultaneously included.
6. Only some of these functions have so far been calculated. E.g. D. M. Ceperley and R. J. Alder, Phys. Rev. Lett. 45, 566 (1980). V. Gupta and A. I. Rajagapol, Phys. Rev. B22, 2792 (1980). I hope that complete tabulations of the properties of uniform thermal ensembles will soon be carried out. The methods are avilable.

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