

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

Walter Kohn^(a)

Theoretische Physik, Eidgenössische Technische Hochschule Hönggerberg, 8093 Zürich, Switzerland
(Received 19 February 1986)

The local-density approximation has been very useful for ground-state calculations. Here an analogous approximation is developed for the ensemble of M lowest states, recently discussed by Theophilou. Algorithms are provided for the exchange-correlation energy, E_{xc}^M , and potential, v_{xc}^M , of ensembles of slowly varying density, $n(r)$. These quantities are highly *nonlocal* functionals of $n(r)$ but calculable in terms of properties of *uniform, thermal* ensembles. Excited-state energies and densities can be obtained.

PACS numbers: 71.10.+x, 31.50.+w, 71.45.-d

The ground-state density-functional theory of Hohenberg, Kohn, and Sham (HKS)^{1,2} was formally extended by Theophilou³ 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 $1/M$. (I shall call such an ensemble an equiensemble.) 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, $E_{xc}^M[n(r')]$ and $v_{xc}^M(r, [n(r')])$, 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):

$$E_{xc}[n(r')] = \int e_{xc}(n(r')) dr', \quad (1)$$

$$v_{xc}(r) = [de_{xc}(n)/dn]_{n=n(r)}, \quad (2)$$

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 equiensemble. A complete manuscript has been submitted elsewhere.

I remark first of all that expressions for E_{xc}^M and v_{xc}^M analogous to (1) and (2) do *not* exist. The reason is that, for given M , the contribution of a volume element dr to E_{xc}^M 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 equiensemble. This approximation is 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 equiensemble with a canonical ensemble of

appropriate temperature θ . Temperature ensembles were first discussed by Mermin,⁴ and local-density approximations for E_{xc}^θ and v_{xc}^θ , quite analogous to (1) and (2) *do* exist.² However, the temperature θ of the canonical ensemble equivalent to the equiensemble 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 noninteracting [Kohn-Sham (KS)] canonical ensemble which is thermodynamically equivalent to the noninteracting (KS) ensemble of M states is different from θ .

The 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 noninteracting electron gases, of the density n and temperature θ' . (The subscript s denotes noninteracting and the subscript l differentiation with respect to temperature.) (a) The entropies per unit volume, $\sigma^{\theta'}(n)$ and $\sigma_s^{\theta'}(n)$, and their temperature derivatives, $\sigma_l^{\theta'}(n)$ and $\sigma_{s,l}^{\theta'}(n)$. (b) The exchange-correlation plus kinetic energy per unit volume, $e^{\theta'}(n)$, and its temperature derivative, $e_l^{\theta'}(n)$. (c) The kinetic energy per unit volume of a noninteracting system, $t_s^{\theta'}(n)$, and its temperature derivative, $t_{s,l}^{\theta'}(n)$.

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

$$k \ln M = \int \sigma^\theta(n(r)) dr; \quad (3)$$

$$k \ln M = \int \sigma_s^{\theta_s}(n(r)) dr.$$

(3) Construct the effective one-particle potential

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

where v_{xc}^M is given by the following expression:

$$v_{xc}^M = \left[\frac{\partial}{\partial n} [e^\theta(n) - t_s^{\theta_s}(n)] \right]_{n=n(r)} + \frac{\partial \theta}{\partial n(r)} \int e_l^\theta(n(r')) dr' - \frac{\partial \theta_s}{\partial n(r)} \int t_{s,l}^{\theta_s}(n(r')) dr', \quad (5)$$

with

$$\frac{\partial \theta}{\partial n(r)} = - \left[\frac{\partial \sigma_l^\theta(n)}{\partial n} \right]_{n=n(r)} \left[\int \sigma_l^\theta(n(r')) dr' \right]^{-1} \quad (6)$$

and

$$\frac{\partial \theta_s}{\partial n(r)} = - \left[\frac{\partial \sigma_{s,l}^{\theta_s}(n)}{\partial n} \right]_{n=n(r)} \left[\int \sigma_{s,l}^{\theta_s}(n(r')) dr' \right]^{-1}. \quad (7)$$

(4) Solve the KS single-particle equations

$$\left[-\frac{1}{2} \nabla^2 + v_{\text{eff}}^M(r) - \epsilon_i \right] \phi_i^M(r) = 0. \quad (8)$$

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

(6) If $n'(r) = n(r)$, 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 equiensemble as follows. Let $E_{s,m}$ ($m = 1, \dots, M$) be the energies of the M lowest KS states. Then

$$E^M = \text{Av}(E_{s,m}) - \frac{1}{2} \int \frac{n(r)n(r')}{|r-r'|} dr dr' - \int v_{xc}^M(r)n(r) dr + \int \{e^\theta(n(r)) - t_s^{\theta_s}(n(r))\} dr, \quad (9)$$

where $\text{Av}(\dots)$ denotes an unweighted average over m .

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.

I express my thanks to the faculty and staff of the Institute for Theoretical Physics of the Eidgenössische Technische Hochschule Hönggerberg for their warm hospitality and for providing a very stimulating environment. This work was supported in part by the National Science Foundation, Grant No. DMR 83-10117.

(a)Permanent address: Department of Physics, University of California, Santa Barbara, Santa Barbara, Cal. 93106.

¹P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

²W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

³A. K. Theophilou, J. Phys. C **12**, 5419 (1979).

⁴N. D. Mermin, Phys. Rev. **137**, A1441 (1965).

⁵When there is a degeneracy, all states of a multiplet are to be simultaneously included.

⁶Only some of these functions have so far been calculated. For example, see D. M. Ceperley and R. J. Alder, Phys. Rev. Lett. **45**, 566 (1980); V. Gupta and A. I. Rajagopal, Phys. Rev. B **22**, 2792 (1980). I hope that complete tabulations of the properties of uniform thermal ensembles will soon be carried out. The methods are available.