Kohn-Sham method as a free-energy minimization at infinite temperature

Robert G. Parr and Y. Alexander Wang

Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599

(Received 9 August 1996)

Given an electronic system in its ground state, having N electrons moving in the field of nuclei generating a potential v_0 and accurate electron density ρ_0, it is demonstrated that the exact Kohn-Sham equations result from a minimization with respect to ρ, at some very high temperature θ, of a free energy functional $A^\theta[\rho,\rho_0] = T_s[\rho] + \langle \rho|v_0 \rangle + J[\rho](1-1/N) - \theta S[\rho,\rho_0]$, where $S[\rho,\rho_0] = -\langle \rho \ln(\rho/\rho_0) \rangle$. The infinite-$\theta$ minimum of A^θ is, within an error so far found to be less than the correlation energy, equal to the total electronic energy of the system. [S1050-2947(97)03404-5]

PACS number(s): 31.15.Ew, 31.25.Eb

The object of concern is the ground state of some electronic system with a fixed number of electrons N in the Born-Oppenheimer approximation, with the electrons moving in an external potential due to the atomic nuclei, $v_0(\mathbf{r})$. The Kohn-Sham (KS) equations for determining the KS orbitals $\{\phi_i\}$, the KS orbital energies $\{\varepsilon_i\}$, and the *exact* ground-state electron density $\rho_0(\mathbf{r})$ are [1,2]

$$[-\tfrac{1}{2}\nabla^2 + v_{\text{eff}}^{\text{KS}}(\mathbf{r})]\phi_i = \varepsilon_i \phi_i \qquad (1)$$

with

$$\sum_{i=1}^{N} |\phi_i|^2 = \rho(\mathbf{r}) \qquad (2)$$

and

$$v_{\text{eff}}^{\text{KS}}(\mathbf{r}) = v_{\text{eff}}^{\text{KS}}[\rho(\mathbf{r})] = v_0(\mathbf{r}) + v_J(\mathbf{r}) + v_{\text{xc}rs}(\mathbf{r}), \qquad (3)$$

where

$$v_J(\mathbf{r}) = v_J[\rho(\mathbf{r})] = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\tau' \qquad (4)$$

and

$$v_{\text{xc}}(\mathbf{r}) = v_{\text{xc}}[\rho(\mathbf{r})] = \frac{\delta E_{\text{xc}}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})}. \qquad (5)$$

Here $E_{\text{xc}}[\rho(\mathbf{r})]$ is the nonclassical part of the electron-electron repulsion-energy functional $V_{\text{ee}}[\rho(\mathbf{r})]$ plus $\{T[\rho(\mathbf{r})] - T_s[\rho(\mathbf{r})]\}$, where $T[\rho]$ is the kinetic-energy functional for the interacting system with density $\rho(\mathbf{r})$ and $T_s[\rho]$ is the kinetic-energy functional for the corresponding noninteracting (no electron-electron repulsion) system with the same density,

$$T_s[\rho(\mathbf{r})] = \sum_{i=1}^{N} \langle \phi_i | -\tfrac{1}{2}\nabla^2 | \phi_i \rangle. \qquad (6)$$

The potential $v_{\text{eff}}^{\text{KS}}$ is unique (up to an arbitrary constant) and multiplicative. The self-consistent solution of Eqs. (1)–(5) achieves the minimization of the energy functional

$$E[\rho(\mathbf{r})] = T_s[\rho(\mathbf{r})] + \langle \rho(\mathbf{r})|v_0 \rangle + J[\rho(\mathbf{r})] + E_{\text{xc}}[\rho(\mathbf{r})]. \qquad (7)$$

At the solution point, $\rho(\mathbf{r}) \equiv \rho_0(\mathbf{r})$, and

$$E[\rho_0(\mathbf{r})] = \sum_{i=1}^{N} \varepsilon_i - J[\rho_0(\mathbf{r})] + \{E_{\text{xc}}[\rho_0(\mathbf{r})] - \langle \rho_0(\mathbf{r})|v_{\text{xc}}[\rho_0(\mathbf{r})]\rangle\}. \qquad (8)$$

A convenient and physical resolution of E_{xc} is [3]

$$E_{\text{xc}}[\rho] = G_{\text{xc}}[\rho] - (1/N)J[\rho]. \qquad (9)$$

Then, Eqs. (3), (7), and (8) become

$$v_{\text{eff}}^{\text{KS}}[\rho] = v_0(\mathbf{r}) + v_J(\mathbf{r})(1-1/N) + v_g[\rho], \qquad (10)$$

$$E[\rho] = T_s[\rho] + \langle \rho|v_0 \rangle + J[\rho](1-1/N) + G_{\text{xc}}[\rho], \qquad (11)$$

and

$$E[\rho_0] = \sum_{i=1}^{N} \varepsilon_i - J[\rho_0](1-1/N) + \{G_{\text{xc}}[\rho_0] - \langle \rho_0|v_g \rangle\}, \qquad (12)$$

where

$$v_g(\mathbf{r}) = v_g[\rho(\mathbf{r})] = \frac{\delta G_{\text{xc}}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})}. \qquad (13)$$

Separating out of the Fermi-Amaldi J/N term causes $v_g(\mathbf{r})$ to have a much shorter range than $v_{\text{xc}}(\mathbf{r})$ [3]. $G_{\text{xc}}[\rho]$ and $v_g[\rho]$ are universal functionals of ρ. Mastery of $G_{\text{xc}}[\rho]$ is the fundamental problem of density-functional theory.

Given an accurate ρ_0 for a given v_0 (determined by conventional quantum-chemical methods or otherwise), $v_{\text{eff}}^{\text{KS}}[\rho_0]$ and hence $v_g[\rho_0]$ can be determined by a brute-force inversion of Eqs. (1) and (2) with ρ set equal to ρ_0. This was demonstrated some years ago [4]. It is not easy to do, but special tricks can help [5]. Typical of recent works exploiting such methods are the paper of Gritsenko, van Leeuwen, and Baerends [6]. As data on more and more accurate $v_g[\rho_0]$ are accumulated, methods from the theory of neural net-

TABLE I. Kohn-Sham quantities (in a.u.) for three atoms. The Zhao-Parr method is described in Ref. [10], and the ''exact'' values of the Kohn-Sham quantities from the Zhao-Parr method are taken from Refs. [3] and [10–12]. For He, Be, and Ne, the temperature θ values employed were 700, 9000, and 16 000, respectively.

Kohn-Sham quantity	He		Be		Ne	
	Zhao-Parr	This work	Zhao-Parr	This work	Zhao-Parr	This work
$T_s[\rho]$	2.867	2.867	14.593	14.591	128.625	128.578
ε_{1s}	−0.9039	−0.9038	−4.2142	−4.2152	−30.812	−30.800
ε_{2a}			−0.3384	−0.3374	−1.654	−1.651
ε_{2p}					−0.797	−0.795
$J[\rho]$	2.050	2.050	7.220	7.219	66.086	66.059
$V_{ne}[\rho]$	−6.753	−6.753	−33.708	−33.705	−311.15	−311.08
$\langle \rho|v_g \rangle$	0.029	0.029	−0.819	−0.819	−6.173	−6.068
$\langle \rho|v_{xc} \rangle$	−2.021	−2.021	−4.429	−4.428	−19.39	−19.28
$E[\rho]$[a]	−2.833	−2.832	−14.518	−14.519	−129.213	−129.122

[a]The Parr-Ghosh formula has been used for $E[\rho]$, as described in the text: Eqs. (20) and (26). Accurate $E[\rho]$ values [15] for the three atoms are −2.904, −14.667, and −128.938, respectively.

works may even be used to instruct the computer to generate better and better approximate representations of the exact $v_g[\rho]$ [7].

A particularly efficient way to accomplish the inversion $\rho_0 \rightarrow v_g$ has recently been developed, based on the Percus-Levy constrained search procedure for determining $T_s[\rho_0]$ [8,9]. That is,

$$T_s[\rho_0] = \min_{D \rightarrow \rho_0} \langle D|\hat{T}|D \rangle, \qquad (14)$$

where D is a Slater determinant of N orthonormal orbitals. At the solution point, the orbitals are the KS orbitals. The equations for determining the orbitals must be just Eq. (1), as can be seen by performing the minimization of Eq. (14), imposing the local constraint

$$\rho(\mathbf{r}) - \rho_0(\mathbf{r}) \equiv 0, \qquad (15)$$

with a point-dependent Lagrange multiplier $v_{\mathrm{eff}}^{\mathrm{KS}}(\mathbf{r})$. This implies the just-described brute-force inversion method. However, one can be more explicit, by enforcing Eq. (15) with the equivalent global constraint [10]

$$C[\rho,\rho_0] \equiv \frac{1}{2} \int \int \frac{[\rho(\mathbf{r})-\rho_0(\mathbf{r})][\rho(\mathbf{r}')-\rho_0(\mathbf{r}')]}{|\mathbf{r}-\mathbf{r}'|} d\tau \, d\tau'$$
$$= 0. \qquad (16)$$

Adopting the partition exhibited in Eqs. (10) and (11), requiring the orthonormality of the orbitals, and attaching a Lagrange multiplier to Eq. (16), give, for the nonclassical part of the effective potential,

$$v_g^\lambda(\mathbf{r}) = \lambda \frac{\delta C[\rho,\rho_0]}{\delta\rho(\mathbf{r})} = \lambda v_c(\mathbf{r}) = \lambda \int \frac{\rho(\mathbf{r})-\rho_0(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\tau'. \qquad (17)$$

Solving the resultant KS-like equations for a fixed λ, with a sufficiently large value of λ, constitutes the Zhao-Parr method [10]. This is straightforward to apply, and gives very good results for all KS quantities [3,10,11]. For an exact ρ_0, one has, accurately [7,10],

$$v_g[\rho_0] = \lim_{\lambda\rightarrow\infty} v_g^\lambda(\mathbf{r}) = \lim_{\lambda\rightarrow\infty} \lambda v_c^\lambda(\mathbf{r})$$
$$= \lim_{\lambda\rightarrow\infty} \lambda \int \frac{\rho^\lambda(\mathbf{r})-\rho_0(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\tau', \qquad (18)$$

where ρ^λ is the solution of the approximate KS equations having v_g replaced by v_g^λ. A few numerical results [11] are presented in Table I. The total electronic energy cannot be computed from this scheme only, since a knowledge of v_g alone does not imply a full knowledge of G_{xc}. On the other hand, with the assumption [3]

$$G_{\mathrm{xc}}[\rho_0] = \langle \rho_0|v_g \rangle, \qquad (19)$$

Eq. (12) becomes the Parr-Ghosh formula for the total energy [3],

$$E[\rho] = \sum_{i=1}^{N} \varepsilon_i - J[\rho](1-1/N). \qquad (20)$$

The error in this formula has been shown to be less than the correlation energy [3]. A more elaborate approximation cuts this error by about one-half [12].

Now begin again, with an alternative to Eq. (16), an entropy-deficiency constraint from information theory [13],

$$S[\rho,\rho_0] \equiv - \left\langle \rho(\mathbf{r})\ln\frac{\rho(\mathbf{r})}{\rho_0(\mathbf{r})} \right\rangle + \{\langle\rho\rangle-\langle\rho_0\rangle\} = 0. \qquad (21)$$

The maximum value of $S[\rho,\rho_0]$ is zero, which occurs if and only if $\rho \equiv \rho_0$. So, attaching a Lagrange multiplier $-\theta$ to this constraint, there now results

$$v_g^\theta(\mathbf{r}) = -\theta \frac{\delta S[\rho,\rho_0]}{\delta\rho(\mathbf{r})} = -\theta v_s(\mathbf{r}) = \theta \ln\frac{\rho(\mathbf{r})}{\rho_0(\mathbf{r})}. \qquad (22)$$

Again the multiplier must be infinity at the solution point, and one has

$$v_g[\rho_0] = \lim_{\theta\to\infty} v_g^\theta(\mathbf{r}) = \lim_{\theta\to\infty}\{-\theta v_s^\theta(\mathbf{r})\} = \lim_{\theta\to\infty}\theta\ln\frac{\rho^\theta(\mathbf{r})}{\rho_0(\mathbf{r})},$$
(23)

where ρ^θ is the solution of the KS-like equation, with v_g^θ replacing v_g. There is a difficulty in the implementation of this procedure: The computed v_g^θ begins to exhibit wild oscillatory behavior when r is very large and v_g has decayed to almost zero [14]. What one does is simply set v_g^θ equal to zero beyond such a point. A peculiar characteristic of the present scheme is that, while the computed v_g^θ is truly excellent, the cutoff in it produces in most cases a negative value of the quantity $\langle\rho|v_g\rangle$, in apparent contradiction with the necessarily non-negative value of the total $-\theta S[\rho,\rho_0]$.

Results are given in Table I. They are seen to duplicate those obtained by the previous method.

In practical calculations for very large θ or λ values, Eq. (23), from the entropy-deficiency constraint of Eq. (21), appears to be more convenient in early stages of iteration, while Eq. (18), from the constraint of Eq. (16), is more convenient near the solution point. More appealingly, the employment of Eq. (23) instead of Eq. (18) produces a converged density ρ much closer to the exact input density ρ_0. Further, the new scheme seems to be particularly satisfying from a physical viewpoint. It amounts to the minimizing with respect to ρ, at constant θ, of a defined Helmholtz-like free-energy functional

$$A^\theta[\rho,\rho_0] = T_s[\rho] + \langle\rho|v_0\rangle + J[\rho](1-1/N) - \theta S[\rho,\rho_0],$$
(24)

followed by requiring θ to go to infinity. Moreover, with Eqs. (21) and (22) and the same normalization for both ρ and ρ_0, one has

$$S[\rho,\rho_0] = \langle\rho|v_s\rangle,$$
(25)

from which follows

$$\lim_{\theta\to\infty} A^\theta[\rho,\rho_0] \equiv A[\rho_0] = \sum_{i=1}^{N}\varepsilon_i - J[\rho](1-1/N).$$
(26)

This is indeed close to the total energy itself, as has been previously demonstrated [3]. The uncertainty associated with Eq. (19) is replaced with the uncertainty as to how close $A[\rho]$ and $E[\rho]$ are to each other. Insofar as the minimization of Eq. (24) as described gives the exact KS procedure and hence all KS quantities exactly, one concludes that *this formulation of the KS procedure is a free-energy minimization at constant temperature, in the limit of infinite temperature.*

This entire discussion has presumed that the exact ground-state density of the system, ρ_0, is known. The extension of the analysis to produce a variational procedure for determining ρ_0 is a prime objective for further work.

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

[2] R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989).

[3] R. G. Parr and S. K. Ghosh, Phys. Rev. A **51**, 3564 (1995).

[4] C.-O. Almbladh and A. C. Pedroza, Phys. Rev. A **29**, 2322 (1984).

[5] For example, Y. Wang and R. G. Parr, Phys. Rev. A **47**, R1591 (1993).

[6] For example, O. V. Gritsenko, R. van Leeuwen, and E. J. Baerends, Phys. Rev. A **52**, 1870 (1995).

[7] D. J. Tozer, V. E. Ingamells, and N. C. Handy, J. Chem. Phys. **105**, 9200 (1996).

[8] J. K. Percus, Int. J. Quantum Chem. **13**, 89 (1978).

[9] M. Levy, Proc. Natl. Acad. Sci. U.S.A. **76**, 6062 (1979).

[10] Q. Zhao and R. G. Parr, Phys. Rev. A **46**, 2337 (1992); J. Chem. Phys. **98**, 543 (1993).

[11] Q. Zhao, R. C. Morrison, and R. G. Parr, Phys. Rev. A **50**, 2138 (1994); R. C. Morrison and Q. Zhao, *ibid.* **51**, 1980 (1995).

[12] R. C. Morrison and R. G. Parr, Phys. Rev. A **53**, R2918 (1996); see also K. Burke, J. P. Perdew, and M. Levy, *ibid.* **53**, R2915 (1996).

[13] For example, see S. B. Sears, Ph.D. dissertation, University of North Carolina at Chapel Hill, 1980.

[14] For an instructive early discussion of such oscillations in model cases, see S. H. Werden and E. R. Davidson, in *Local Density Approximations in Quantum Chemistry and Solid State Physics*, edited by J. P. Dahl and J. Avery (Plenum, New York, 1984), pp. 33–42.

[15] S. J. Chakravorty and E. R. Davidson, J. Phys. Chem. **100**, 616 (1996).