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Construction of exact Kohn-Sham orbitals from a given electron density

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This paper prescribes an orbital construction of the exact local effective potential in the Kohn-Sham self-consistent equations, so that from a given electron density the corresponding exact Kohn-Sham potential and orbitals may be found self-consistently. It also shows the convergence of the method if the system is v representable.

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In the Kohn-Sham formalism [1] of density-functional theory [2], the ground-state electron density $n(\mathbf{r})$ of an interacting system with external potential $v_{\mathrm{ext}}(\mathbf{r})$ is determined self-consistently from the equations (in atomic units throughout the paper)

$$[-\tfrac{1}{2}\nabla^2+w(\mathbf{r})]\varphi_i(\mathbf{r})=\varepsilon_i\varphi_i(\mathbf{r}) \ , \tag{1}$$

$$w(\mathbf{r})=v_{\mathrm{ext}}(\mathbf{r})+v_H(\mathbf{r})+v_{\mathrm{xc}}(\mathbf{r}) \ , \tag{2}$$

$$v_{\mathrm{xc}}(\mathbf{r})=\frac{\delta E_{\mathrm{xc}}[n]}{\delta n(\mathbf{r})} \ , \tag{3}$$

$$v_H(\mathbf{r})=\int d^3r'\frac{n(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} \ . \tag{4}$$

Here

$$n(\mathbf{r})=\sum_i|\varphi_i(\mathbf{r})|^2 \ , \tag{5}$$

where the sum is over the N lowest occupied orbitals.

All we need to know to implement calculations with these equations is the universal exchange-correlation potential $v_{\mathrm{xc}}(\mathbf{r})$, which is defined as the functional derivative of the unknown exchange-correlation energy density functional $E_{\mathrm{xc}}[n]$. However, an orbital construction of $v_{\mathrm{xc}}(\mathbf{r})$ may work equally well, since in the course of the self-consistent Kohn-Sham calculations we always obtain orbitals before we construct the density. Therefore, a knowledge of $v_{\mathrm{xc}}(\mathbf{r})$, constructed either from density or orbitals, is sufficient to deduce the ground-state density.

The inverse question, i.e., given a ground-state density $n(\mathbf{r})$ to find the orbitals and the corresponding effective potential $v_{\mathrm{xc}}(\mathbf{r})$, is also interesting because in some cases the electron density can be found accurately by Monte Carlo simulations, by sophisticated traditional quantum-chemical methods, or by experiment. If one can construct the exact effective Kohn-Sham potential from the density, one will be in a position to better study known or new approximations for the exchange-correlation energy functional (or potential) in density-function theory.

Different approaches have been suggested [3–12,18] to deal with this problem. Some involve varying the parameters in a trial effective potential $w(\mathbf{r})$ to fit a given density [3–5], and some involve minimizing the kinetic energy subject to appropriate constraints [6–8]. In the exchange-only approximation Talman and Shadwick [9] found a local effective central potential for spherically symmetric atoms. Werden and Davidson used the linear response of the effective potential to the change of density in a one-dimensional system in an iterative calculation [10]. Aryasetiawan and Stott solved $N-1$ coupled simultaneous second-order differential equations with care taken to ensure the cusp condition [11] to obtain the

Kohn-Sham orbitals and the effective potential [12,13]. All these methods are restricted to a few small systems like beryllium and neon atoms.

This work presents a general approach for constructing the exact Kohn-Sham orbitals from a given electron density. It is related to the iterative procedure of Werden and Davidson [10] but with the crucial advantage of being applicable to any real large system up to the size that can be handled by today's Kohn-Sham computer programs. It differs from previous works in the following sense: (i) it imposes no constraint on the form of the effective potential as we seek it; (ii) there is no additional parameter such as the Lagrange multiplier which has to be determined in the calculations; (iii) it is exact and general; and (iv) there are no boundary conditions or unoccupied orbitals involved and it is particularly easy to implement.

Because of the one-to-one correspondence between the density $n(\mathbf{r})$ and the effective potential $w(\mathbf{r})$ [except for a trivial additive constant to $w(\mathbf{r})$] we do not need to know the detailed structure of $v_{\mathrm{xc}}(\mathbf{r})$. If we can find one potential $w(\mathbf{r})$ which generates the known density $n(\mathbf{r})$ through Eqs. (1) and (5), we will have found the exact effective potential $w(\mathbf{r})$ and consequently the correct Kohn-Sham orbitals. [This idea was first used by Williams and von Barth [14] and Smith, Jagannathan, and Handler [15] to get $v_{\mathrm{xc}}(\mathbf{r})$ for the helium atom within the Hartree-Fock approximation.]

We rewrite Eq. (1) as

$$\varphi_i(\mathbf{r})=w(\mathbf{r})\frac{1}{\varepsilon_i}\varphi_i(\mathbf{r})+\frac{1}{\varepsilon_i}(-\tfrac{1}{2}\nabla^2)\varphi_i(\mathbf{r})\ . \tag{6}$$

The density constructed from these orbitals is

$$\begin{aligned}\sum_i \varphi_i(\mathbf{r})^*\varphi_i(\mathbf{r})=w(\mathbf{r})&\sum_i\frac{1}{\varepsilon_i}\varphi_i(\mathbf{r})^*\varphi_i(\mathbf{r})\\&+\sum_i\frac{1}{\varepsilon_i}\varphi_i(\mathbf{r})^*(-\tfrac{1}{2}\nabla^2)\varphi_i(\mathbf{r})\ .\end{aligned} \tag{7}$$

Now equating Eq. (7) to the given density $n(\mathbf{r})$, we find

$$w(\mathbf{r})=\frac{n(\mathbf{r})-\sum_i\frac{1}{\varepsilon_i}\varphi_i(\mathbf{r})^*(-\tfrac{1}{2}\nabla^2)\varphi_i(\mathbf{r})}{\sum_i\frac{1}{\varepsilon_i}\varphi_i(\mathbf{r})^*\varphi_i(\mathbf{r})}\ . \tag{8}$$

To solve Eqs. (1) and (8) we make an initial guess $w^0(\mathbf{r})$ for the effective potential $w(\mathbf{r})$ and solve Eq. (1) for the N lowest orbital energies and the orbitals associated with them. Then we construct a new effective potential according to Eq. (8) using the orbitals and orbital energies just found. We go back to Eq. (1) with the newly constructed effective potential, and repeat the procedure until self-consistency is reached. There results the exact effective potential $w(\mathbf{r})$ and Kohn-Sham orbitals. From them will follow the properties of the noninteracting system, including $T_s[n]$.

Denote iteration numbers by superscripts. Then we have

$$[-\tfrac{1}{2}\nabla^2+w^{p-1}(\mathbf{r})]\varphi_i^p(\mathbf{r})=\varepsilon_i^p\varphi_i^p(\mathbf{r})\ . \tag{9}$$

Thus

$$\varphi_i^p(\mathbf{r})^*(-\tfrac{1}{2}\nabla^2)\varphi_i^p(\mathbf{r})=[\varepsilon_i^p-w^{p-1}(\mathbf{r})]\varphi_i^p(\mathbf{r})^*\varphi_i^p(\mathbf{r})\ . \tag{10}$$

Substituting this result into

$$w^p(\mathbf{r})=\frac{n(\mathbf{r})-\sum_i\frac{1}{\varepsilon_i^p}\varphi_i^p(\mathbf{r})^*(-\tfrac{1}{2}\nabla^2)\varphi_i^p(\mathbf{r})}{\sum_i\frac{1}{\varepsilon_i^p}\varphi_i^p(\mathbf{r})^*\varphi_i^p(\mathbf{r})}\ , \tag{11}$$

we obtain

$$\begin{aligned}w^p(\mathbf{r})&=\frac{n(\mathbf{r})-\sum_i\left[1-\frac{w^{p-1}(\mathbf{r})}{\varepsilon_i^p}\right]\varphi_i^p(\mathbf{r})^*\varphi_i^p(\mathbf{r})}{\sum_i\frac{1}{\varepsilon_i^p}\varphi_i^p(\mathbf{r})^*\varphi_i^p(\mathbf{r})}\\&=\frac{n(\mathbf{r})-n^p(\mathbf{r})}{\sum_i\frac{1}{\varepsilon_i^p}\varphi_i^p(\mathbf{r})^*\varphi_i^p(\mathbf{r})}+w^{p-1}(\mathbf{r})\ ,\end{aligned} \tag{12}$$

where

$$n^p(\mathbf{r})=\sum_i\varphi_i^p(\mathbf{r})^*\varphi_i^p(\mathbf{r})\ . \tag{13}$$

That is to say,

$$w^p(\mathbf{r})-w^{p-1}(\mathbf{r})=\frac{n(\mathbf{r})-n^p(\mathbf{r})}{\sum_i\frac{1}{\varepsilon_i^p}\varphi_i^p(\mathbf{r})^*\varphi_i^p(\mathbf{r})}\ . \tag{14}$$

This interesting lemma implies that during the iterative process the density $n^p(\mathbf{r})$ is constantly compared with the given density $n(\mathbf{r})$. As long as there is a difference between them, a new effective potential will result. This feature will drive the calculations eventually to self-consistency if a solution exists. When $w^p(\mathbf{r})=w^{p-1}(\mathbf{r})$, $n^p(\mathbf{r})=n(\mathbf{r})$, and inversely.

As an example of this method, we have carried out a simple calculation for the beryllium atom. We used just six basis functions (two $1s$-type and four $2s$-type Slater orbitals) to expand Kohn-Sham orbitals. Employing an accurate density from Esquivel and Bunge [16], we reach a self-consistency in which we can reproduce the desired density with an error of 0.002 over the range $r=10^{-6}$ to 10. We compute the kinetic energy and find $T_s=14.5947$. This is fairly accurate compared with the result of a more sophisticated calculation [17], 14.5932.

The simple and compact form of Eq. (14) suggests that the function in the denominator of the right-hand side, i.e., the quantity

$$\sum_i\frac{1}{\varepsilon_i}|\varphi_i(\mathbf{r})|^2\ , \tag{15}$$

may be of special interest and worth further studying.

Dr. Zhongxiang Zhou of this laboratory has devised another, similar procedure by summing Eq. (1) without dividing by ε_i.

In summary, we have found an orbital construction of the exact effective potential so that the Kohn-Sham self-consistent equations will decompose a given ground-state electron density into the corresponding noninteracting Kohn-Sham orbitals.

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