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Exact potential-phase relation for the ground state of the C atom

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Exact density-phase relations have been derived for a three-level independent-particle problem. The density can explicitly be written in terms of the phase functions ϑ and φ and their derivatives. The Euler equation of the density-functional theory has been derived for the ground state of the C atom. The one-body potential V can be obtained from the phase functions ϑ and φ. The differential form of the virial theorem of March and Young [Nucl. Phys. **12**, 237 (1959)] has been generalized for particles moving in a common local potential V and having different azimuthal quantum numbers.

I. INTRODUCTION

To obtain the exact functionals of density in the density-functional theory[1] is, without doubt, of fundamental importance. Several approximations have already been used but the exact explicit functionals are still unknown. The first simple approximation to the Euler equation of the density-functional theory was provided by the Thomas-Fermi theory well before the birth of the modern density-functional theory. The exchange-correlation potential of the Kohn-Sham equation was first approximated by Slater[2] then Gáspár,[3] Kohn and Sham[4] by a local-density $n^{1/3}$-type potential.

The existence of the potential of the Kohn-Sham equations as functional of the electron density is guaranteed by the density-functional theory. March and Nalewajski[5] derived an explicit relation between the potential and the density in the Be atom making use of the density-matrix variational method set up by Dawson and March.[6]

A more direct potential relation has recently been presented for the two-level problem.[7] It has turned out that the potential can be explicitly expressed by the phase function θ and its derivatives.

Now, the three-level problem is treated. The density ρ can explicitly be expressed in terms of the phase functions ϑ and φ and their derivatives. To derive the Euler equation the differential form of the virial theorem of March and Young[8] has been generalized. The one-body potential can be written as a function of the phase functions ϑ and φ and their derivatives.

II. EXACT DENSITY-PHASE RELATIONS FOR A THREE-LEVEL INDEPENDENT-PARTICLE PROBLEM

Let us consider a three-level independent-particle problem for an external potential $V(r)$. The ground state of the C atom is an example for this problem. The ground-state density

$$n(r)=2[R_1^2(r)+R_2^2(r)+R_3^2(r)] \tag{2.1}$$

is considered to be spherically symmetric. Provided we apply the usual normalization condition

$$\int_0^\infty R_n^2 4\pi r^2 dr=1, \quad n=1,2,3 \tag{2.2}$$

the density $n(r)$ integrates to 6, the number of electrons in the ground state of C. With a transformation

$$rR_n(r)\longrightarrow\phi_n(r), \quad n=1,2,3$$
$$r\longrightarrow x \tag{2.3}$$

and applying the density $\rho(x)$ defined by

$$2\rho(x)=4\pi x^2 n(x) \tag{2.4}$$

one obtains

$$\rho(x)=4\pi\sum_{i=1}^{3}\phi_i^2(x) \ . \tag{2.5}$$

Applying the transformation of Dawson and March[6] we have

$$\begin{aligned}\phi_1(x)&=(1/\sqrt{2})\rho^{1/2}(x)\sin\vartheta(x)\cos\varphi(x) \ ,\\ \phi_2(x)&=(1/\sqrt{2})\rho^{1/2}(x)\sin\vartheta(x)\sin\varphi(x) \ ,\\ \phi_3(x)&=(1/\sqrt{2})\rho^{1/2}(x)\cos\vartheta(x) \ .\end{aligned} \tag{2.6}$$

The wave functions ϕ_1 and ϕ_2 satisfy the one-body Schrödinger equation

$$\phi_n''+2[\varepsilon_n-V(x)]\phi_n=0, \quad n=1,2 \tag{2.7}$$

where ε_1 and ε_2 are the eigenvalues of the $1s$ and $2s$ electrons. For the wave function ϕ_3 we have

$$\phi_3''+2\left[\varepsilon_3-V-\frac{l(l+1)}{2x^2}\right]\phi_3=0 \ , \tag{2.8}$$

where ε_3 is the eigenvalue of the $2p$ electron and $l=1$. Eliminating the potential V from Eqs. (2.7) and (2.8) we get

$$\phi_1''\phi_2-\phi_1\phi_2''=2(\varepsilon_2-\varepsilon_1)\phi_1\phi_2 \tag{2.9a}$$

and

$$\phi_1''\phi_3-\phi_1\phi_3''=2(\varepsilon_3-\varepsilon_1-1/x^2)\phi_1\phi_3 \ . \tag{2.9b}$$

Applying the transformation (2.6) one obtains the equations

$$\varphi''+(\Gamma'/\Gamma)\varphi'-2\xi\sin(2\varphi)=0 \ , \tag{2.10a}$$

$$\vartheta''+\frac{\rho'}{\rho}\vartheta'-\sin(2\vartheta)\left[\tfrac{1}{2}(\varphi')^2+\left[\varepsilon_3-\varepsilon_1-\frac{1}{x^2}\right]+2\xi\sin^2\varphi\right]=0 \ , \tag{2.10b}$$

where

$$\Gamma=\rho\sin^2\vartheta \ . \tag{2.11}$$

From Eq. (2.10a) the density is given by

$$\rho=\frac{1}{\varphi'\sin^2\vartheta}e^{2\xi h} \ , \tag{2.12}$$

where

$$h=\int^{\vartheta}\frac{\sin(2\varphi)}{\varphi'}dx \tag{2.13}$$

and

$$\xi=(\varepsilon_1-\varepsilon_2)/2 \ . \tag{2.14}$$

Equation (2.10b) leads to the expression

$$\rho=(1/\vartheta')e^{g} \ , \tag{2.15}$$

where

$$g=\int dx\frac{1}{\vartheta'}\left[\varepsilon_3-\varepsilon_1-\frac{1}{x^2}+\tfrac{1}{2}(\varphi')^2+2\xi\sin^2\varphi\right]\sin(2\vartheta)$$

Thus the expressions (2.12) and (2.15) provide the functions ρ explicitly in terms of the phase functions ϑ and φ and their derivatives. It is interesting to note that it is the density ρ that can be eliminated by using the phase functions. The price we have to pay for this is that the density ρ is a function of ϑ' or φ', too. It is worth mentioning that the density can be given by a similar formula in the two-level case. On the other hand, Eqs. (2.10) can be used to determine the phase functions ϑ and φ if ρ'/ρ is known.

III. EXACT EXPLICIT POTENTIAL RELATION

Now, we want to derive the density-potential relation which is the basic aim of the density-functional theory, for this simple three-level problem. The kinetic energy density

$$t=-\phi_1\phi_1''-\phi_2\phi_2''-\phi_3\phi_3''+(2/x^2)\phi_3^2 \tag{3.1}$$

can be expressed as

$$t=-\tfrac{1}{4}\rho''+\frac{1}{8}\frac{(\rho')^2}{\rho}+\tfrac{1}{2}\rho(\vartheta')^2+\tfrac{1}{2}\rho(\sin^2\vartheta)(\varphi')^2+\frac{1}{x^2}\rho\cos^2\vartheta \tag{3.2}$$

using Eqs. (2.6). Another expression for t is

$$t=\rho\left[-\tfrac{1}{8}F^2-\tfrac{1}{4}F'+\tfrac{1}{2}(\vartheta')^2+\tfrac{1}{2}(\varphi')^2\sin^2\vartheta+\frac{1}{x^2}\cos^2\vartheta\right] , \tag{3.3}$$

where

$$F=\rho'/\rho \ . \tag{3.4}$$

The differential form of the virial theorem derived by March and Young[8] is generalized for particles moving in a common local potential $V(x)$ and having different azimuthal quantum numbers l_k. It is shown in the Appendix that

$$t'=-\tfrac{1}{8}\rho'''-\tfrac{1}{2}\rho V'+\tfrac{1}{2}\sum_k l_k(l_k+1)\left[\frac{\rho_k'}{x^2}-\frac{\rho_k}{x^3}\right] , \tag{3.5}$$

where

$$\rho_k=\phi_k^*\phi_k \ . \tag{3.6}$$

In the three-level case:

$$t'=-\tfrac{1}{8}\rho'''-\tfrac{1}{2}\rho V'+2\left[\frac{(\phi_3^2)'}{x^2}-\frac{\phi_3^2}{x^3}\right] . \tag{3.7}$$

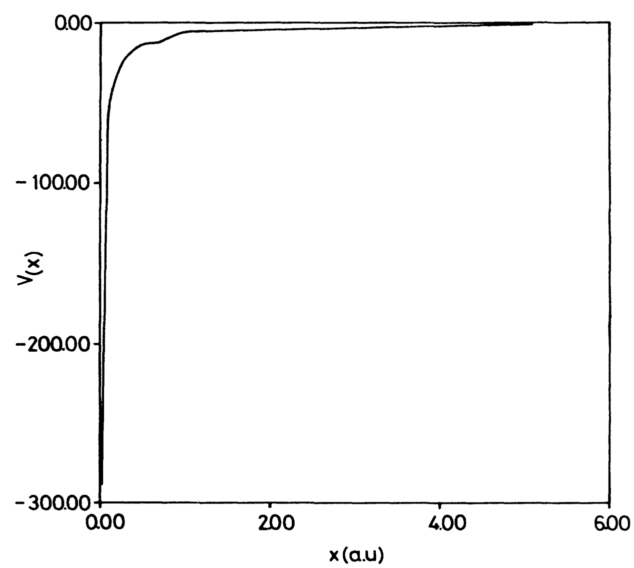

FIG. 1. Hartree-Fock potential for C.

Combining Eqs. (3.2), (3.3), (3.7), and (2.10) we have

$$V=\tfrac{1}{8}F^2+\tfrac{1}{4}F'-\tfrac{1}{2}(\vartheta')^2-\tfrac{1}{2}(\vartheta')^2\sin^2\vartheta + (\cos^2\vartheta)\left[2\eta-\frac{1}{x^2}\right]-2\xi\sin^2\varphi\sin^2\vartheta+\varepsilon_1 \; , \tag{3.8}$$

where

$$\eta=\tfrac{1}{2}(\varepsilon_3-\varepsilon_1) \; . \tag{3.9}$$

In this way one arrives at an exact, explicit relation for V. However, we get the potential-phase relation instead of the potential-density relation. It is one of the most important conclusions that explicit relations can be more conveniently and elegantly given using the phase functions ϑ and φ instead of ρ. It is worth emphasizing that Eq. (3.8) is the Euler equation of the density-functional theory.

IV. DISCUSSION

Equations (2.10) and (3.8) are the main results of the paper. If ρ'/ρ is known for a three-level ground-state system the phase functions ϑ and φ can be obtained by solving Eqs. (2.10). The potential $V(x)$ can be determined using Eqs. (3.8).

Figure 1 shows the Hartree-Fock potential $V_{\mathrm{HF}}(x)$ for the ground state of C. Here, instead of solving the (2.10) nonlinear coupled equations, the Hartree-Fock[9] solutions using Eqs. (2.6) have been used to obtain the potential $V_{\mathrm{HF}}(x)$ of Eqs. (3.8).

Ions having the same ground-state electron configuration can be similarly treated.

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APPENDIX

Here we discuss the differential form of the virial theorem for particles moving in a common spherically symmetric potential $V(r)$.

The differential form of the virial theorem for particles moving in a one-dimensional common local potential has been derived by March and Young.[8] Now a generalization of this theorem for particles in a common spherically symmetric potential $V(r)$ is presented. The procedure used by March and Young is followed.

The Schrödinger equations of particles in a potential $V(r)$

$$-\frac{1}{2}\frac{d^2\phi_k}{dr^2}+\frac{l_k(l_k+1)}{2r^2}\phi_k+V\phi_k=\varepsilon_k\phi_k \tag{A1}$$

can be rewritten as

$$\frac{d^2\phi_k^*(r')}{(dr')^2}\phi_k(r)-\phi_k^*(r')\frac{d^2\phi_k(r)}{dr^2}=2\left[V(r')-V(r)+\frac{l_k(l_k+1)}{2}\left[\frac{1}{(r')^2}-\frac{1}{r^2}\right]\right]\phi_k^*(r')\phi(r) \; . \tag{A2}$$

With the notation

$$\rho(r',r)=\sum_k \phi_k^*(r')\phi_k(r) \tag{A3}$$

and

$$\rho_k(r',r)=\phi_k^*(r')\phi_k(r) \; , \tag{A4}$$

Eq. (A2) can be written as

$$\frac{\partial^2\rho}{\partial(r')^2}-\frac{\partial^2\rho}{\partial r^2}=2[V(r')-V(r)]\rho + \sum_k l_k(l_k+1)\left[\frac{1}{(r')^2}-\frac{1}{r^2}\right]\rho_k \; . \tag{A5}$$

The energy E is given by

$$E=-\tfrac{1}{2}\int\left[\frac{\partial^2\rho(r',r)}{\partial r^2}\right]_{r'=r}dr + \tfrac{1}{2}\sum_k l_k(l_k+1)\int\frac{\rho_k(r,r)}{r^2}dr+\int\rho(r,r)V(r)dr \; . \tag{A6}$$

Following Naqvi's[10] procedure the transformation

$$\xi=\tfrac{1}{2}(r'+r), \quad \eta=\tfrac{1}{2}(r'-r) \; , \tag{A7}$$

leads to the equation

$$\frac{\partial^2\rho}{\partial\xi\,\partial\eta}=2[V(\xi+\eta)-V(\xi-\eta)]\rho + \sum_k l_k(l_k+1)\left[\frac{1}{(\xi+\eta)^2}-\frac{1}{(\xi-\eta)^2}\right]\rho_k \; . \tag{A8}$$

Expanding ρ and ρ_k about the point $\eta=0$

$$\rho(\xi,\eta)=\rho(\xi)+\sum_{j=1}^{\infty}\eta^{2j}a_{2j}(\xi) \tag{A9}$$

and

$$\rho_k(\xi,\eta)=\rho_k(\xi)+\sum_{j=1}^{\infty}\eta^{2j}b_{2j}^{k}(\xi) \; , \tag{A10}$$

where

$$\rho(\xi)=\rho(\xi,0) \tag{A11}$$

and

$$\rho_k(\xi)=\rho_k(\xi,0) \; . \tag{A12}$$

By substituting the expressions (A9)–(A12) into (A8) it is easy to see that

$$\frac{da_2}{d\xi}=2\frac{dV}{d\xi}\rho(\xi)-2\sum_k \frac{l_k(l_k+1)}{\xi^3}\rho_k(\xi) . \quad \text{(A13)}$$

Using (A6), (A9), and (A10) the kinetic energy T can be given by

$$T=-\frac{1}{4}\int \left[\frac{1}{2}\rho''+a_2-2\sum_k \frac{l_k(l_k+1)}{x^2}\rho_k\right]dx . \quad \text{(A14)}$$

The kinetic energy density is given by

$$t=-\frac{1}{8}\rho''-\frac{1}{2}\int \rho V' dx + \frac{1}{2}\sum_k l_k(l_k+1)\left[\frac{\rho_k}{x^2}+\int \frac{\rho_k}{x^3}dx\right] , \quad \text{(A15)}$$

applying Eq. (A13). By differentiation we get

$$t'=-\frac{1}{8}\rho'''-\frac{1}{2}\rho V'+\frac{1}{2}\sum_k l_k(l_k+1)\left[\frac{\rho_k'}{x^2}-\frac{\rho_k}{x^3}\right] , \quad \text{(A16)}$$

which is the generalized form of the differential virial theorem of March and Young.[8] For particles having zero angular momentum the original form of March and Young is obtained

$$t'=-\frac{1}{8}\rho'''-\frac{1}{2}\rho V' . \quad \text{(A17)}$$

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