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Exact density-potential relation for the ground state of the Be atom

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The exact ground-state density $n(r)$ of the Be atom can be generated, at least in principle, from a local one-body potential energy $V(r)$, which must include however an appropriate contribution from exchange and correlation interactions. Here an exact relation between $n(r)$ and this given $V(r)$ is exhibited by making use of the density matrix variational method set up by Dawson and March for two occupied levels in a one-dimensional system.

I. INTRODUCTION

A basic aim of modern density-functional theory[1–3] is to obtain an explicit relation from which to calculate the ground-state electron density $n(\mathbf{r})$. In Thomas-Fermi theory, the forerunner of modern density-functional theory, this is achieved for electrons moving in a common one-body potential energy $V(\mathbf{r})$ as[4]

$$n(\mathbf{r})=\frac{8\pi}{3h^3}(2m)^{3/2}[\mu-V(\mathbf{r})]^{3/2} \tag{1.1}$$

in classically allowed regions, and $n(\mathbf{r})=0$ where motion is classically forbidden.

That this relation (1.1) can be transcended by taking account of density gradients was already clear to von Weizsäcker.[5,6] But inclusion of such low-order density gradient corrections is inadequate in, say, closed-shell atoms, for the density $n(r)$ thereby generated does not reflect the atomic shell structure in an atom such as Ar.

Therefore, in the present work, by focusing solely on a simple atom, Be, in its ground state, we shall set up a formally exact method of calculating the density $n(r)$, given a one-body potential energy $V(r)$ in which both $1s$ and $2s$ electrons move. That such a common potential should underlie electron density calculations in atoms, molecules, and solids was already clear to Slater,[7] but the $V(\mathbf{r})$ he proposed was simply the sum of the Hartree potential generated by the nuclear framework and $n(\mathbf{r})$ itself, plus a local-density $[n(\mathbf{r})]^{1/3}$ type potential from exchange effects. Gombás and others[8] had earlier proposed adding a contribution to Thomas-Fermi-Dirac theory from local-density approximations to the correlation energy. A formally exact definition of $V(\mathbf{r})$ was given by Kohn and Sham[9] but this involves a functional derivative with respect to $n(\mathbf{r})$ of the, as yet unknown, exchange and correlation energy functional $E_{\mathrm{xc}}[n]$. All that is important for the present study is that a formally exact central potential energy exists which will generate the true electron density $n(r)$ of the ground state of Be. This will be assumed below; given that, the density-functional program of obtaining $n(r)$ exactly given $V(r)$ is pushed through to a final, exact, though still somewhat complicated n-V relation.

To complete this Introduction, we merely comment briefly on the relation of the Be atom density $n(r)$ to an equivalent two-level problem in one dimension. Thus, given $V(r)$, we can obviously calculate the radial wave functions $R_1(r)$ and $R_2(r)$ of the $1s$ and $2s$ electrons, with corresponding eigenvalues ϵ_1 and ϵ_2 from the Schrödinger equation. Provided we adopt the normalization $\int_0^\infty R_n^2 4\pi r^2 dr=1$, the ground-state density is evidently

$$n(r)=2[R_1^2(r)+R_2^2(r)] \; . \tag{1.2}$$

Instead of setting up the off-diagonal density-matrix generalization of Eq. (1.2) for Be, we shall find it economical below to transform instead the calculations of Dawson and March[10] in which a variational density matrix was set up for two occupied levels in a one-dimensional system.

To make contact with their work, one needs only to make the transformation

$$\begin{aligned} &rR_n(r)\rightarrow\phi_n(r), \quad n=1,2 \\ &r\rightarrow x \; . \end{aligned} \tag{1.3}$$

It must then be noted that the "one-dimensional density $\rho(x)$" which they calculate is in fact such that

$$\rho(x)=4\pi[\phi_1^2(x)+\phi_2^2(x)] \; . \tag{1.4}$$

Once one has calculated $\rho(x)$ from the Dawson-March variational procedure, the Be atom density $n(r)$ given in Eq. (1.2) is clearly related to this one-dimensional density $\rho(r)$ by

$$4\pi r^2 n(r)=2\rho(r) \; . \tag{1.5}$$

If $\int_0^\infty \rho(r)dr=2$, as we shall assume, then from Eq. (1.5) the density $n(r)$ integrates to 4, as it must for the ground state of Be.

In Sec. II, we first clarify, and then manipulate, the Dawson-March equations to yield an explicit relation between $n(r)$ and the given $V(r)$ which, as we have stressed above, involves many-electron contributions which are not yet known exactly. However, the procedure given in Sec. II relates $n(r)$ exactly for Be to the given $V(r)$. It is relevant in connection with Sec. II to mention the work of Capitani *et al.*,[11] which is closely related to the work of Dawson and March.[10] Capitani *et al.* also, in fact, discuss briefly the relationship between spherical and one-dimensional problems.

II. EXACT DENSITY-POTENTIAL RELATION FOR A TWO-LEVEL ONE-DIMENSIONAL CASE

Consider a two-level, one-dimensional, independent-particle problem for an external potential $V(x)$, e.g., the harmonic oscillator with the first two states occupied, as discussed in the Appendix B. Following Ref. 10, we adopt polar coordinates in which to express the one-body orbitals ϕ_1 and ϕ_2 as well as the single-particle density matrix $\gamma(x',x)$, in terms of the density $\rho(x)$, given simply by $\rho(x)=\gamma(x,x)=2\phi_1^2+2\phi_2^2$:

$$\begin{aligned} 2^{1/2}\phi_1(x)&=\rho^{1/2}\cos\theta(x)\ ,\\ 2^{1/2}\phi_2(x)&=\rho^{1/2}\sin\theta(x)\ , \end{aligned} \tag{2.1}$$

and

$$\gamma(x',x)=\sqrt{\rho(x')}\sqrt{\rho(x)}\cos[\theta(x')-\theta(x)]\ . \tag{2.2}$$

Hence one obtains the expression for the kinetic energy density

$$\begin{aligned} t(x)&=-\frac{1}{2}\left.\frac{\partial^2\gamma(x',x)}{\partial x^2}\right|_{x'=x}\\ &=-\tfrac{1}{4}\rho''(x)+\frac{1}{8}\frac{(\rho')^2}{\rho}+\tfrac{1}{2}\rho(\theta')^2\ , \end{aligned} \tag{2.3}$$

satisfying the one-dimensional virial theorem[12,13]

$$t(x)=-\tfrac{1}{8}\rho''-\tfrac{1}{2}\int^x \rho V'dt\ . \tag{2.4}$$

Combining Eqs. (2.3) and (2.4) immediately yields

$$u=(\theta')^2=\frac{1}{4}\left[\frac{\rho''}{\rho}-\left[\frac{\rho'}{\rho}\right]^2\right]-\frac{1}{\rho}\int^x \rho V'dt\ , \tag{2.5}$$

which gives $(\theta')^2$ in terms only of ρ and V.

The equations relating $\rho=\chi^2$ and V for the the two-level independent-particle problem in one dimension have been derived from the Euler-Lagrange equations corresponding to a minimum of the appropriate energy functional for the two-level case:

$$E_2[\rho,\theta]=\int (t+V\rho)dx\ ,$$

subject to the density-matrix idempotency constraints

$$\begin{aligned} &\int \rho\cos(2\theta)\,dx=\int \rho\sin^2\theta\,dx=2\ ,\\ &\int \rho\sin\theta\cos\theta\,dx=0\ . \end{aligned} \tag{2.6}$$

In this way, one obtains the equations[10]

$$\tfrac{1}{2}\theta''+\left[\frac{\chi'}{\chi}\right]\theta'=\xi\sin(2\theta)-\eta\cos(2\theta) \tag{2.7}$$

and

$$-\tfrac{1}{2}\chi''+[\tfrac{1}{2}(\theta')^2+V]\chi=[\lambda+\xi\cos(2\theta)+\eta\sin(2\theta)]\chi\ , \tag{2.8}$$

where $\chi^2=\rho$, and λ, ξ, and η are Lagrange undetermined multipliers.

Clearly, for given exact orbitals ϕ_1 and ϕ_2 satisfying the one-body Schrödinger equations

$$\phi_i''+2[\epsilon_i-V(x)]\phi_i=0;\ \ i=1,2 \tag{2.9}$$

the idempotency conditions (2.6) are automatically fulfilled by the orthonormality of orbitals. Therefore we can alternatively derive Eqs. (2.7) and (2.8) using the Schrödinger equations. This allows the following identification of the Lagrange multipliers:

$$\eta=0,\ \ \xi=(\epsilon_1-\epsilon_2)/2,\ \ \lambda=(\epsilon_1+\epsilon_2)/2\ . \tag{2.10}$$

As demonstrated by Dawson and March,[10] differentiation of Eq. (2.8) and substitution of Eq. (2.7) yields

$$\theta''\theta'+\frac{\chi'}{\chi}(\theta')^2+\frac{1}{2}\left[V'-\frac{1}{2}\left[\frac{\chi''}{\chi}\right]'\right]=0\ , \tag{2.11}$$

which can be transformed into a solvable Bernoulli differential equation for $u=(\theta')^2$, with general solution

$$\begin{aligned} u&=\frac{C_1}{\chi^2}-\frac{1}{\chi^2}\int^x\left[\frac{\chi'\chi''}{2\chi^2}-\frac{\chi'''}{2\chi}+V'\right]\chi^2dt\\ &=\frac{C_1}{\chi^2}+\frac{1}{2\chi^2}\int^x\left[\frac{\chi''}{\chi}\right]'\chi^2dt-\frac{1}{\chi^2}\int^x\chi^2V'dt\ . \end{aligned} \tag{2.12}$$

A simple integration by parts given Eq. (2.5), since

$$\begin{aligned} u&=\frac{C_1}{\chi^2}+\frac{1}{2}\frac{\chi''}{\chi}-\frac{1}{2}\left[\frac{\chi'}{\chi}\right]^2-\frac{1}{\chi^2}\int^x\chi^2V'dt\\ &=\frac{C_1}{\rho}+\frac{1}{4}\left[\frac{\rho''}{\rho}-\left[\frac{\rho'}{\rho}\right]^2\right]-\frac{1}{\rho}\int^x\rho V'dt\ , \end{aligned} \tag{2.13}$$

and hence Eq. (2.5) is regained provided $C_1=0$. Therefore Eq. (2.20) of Ref. 10 represents basically the use of the virial theorem (2.4) in expressing the kinetic energy density for such a two-level problem.

Equations (2.7), (2.8), and (2.11) allow, after a somewhat lengthy algebraic manipulation, θ to be eliminated completely, and in this way one arrives at an exact equation explicitly relating ρ and V. This achieves then a basic aim of density-functional theory in the two-level case. The explicit form of this equation is

$$\begin{aligned} u^3&+\left[4F+\frac{1}{4}\left[\frac{\rho'}{\rho}\right]^2\right]u^2\\ &+\left[4(F^2-\xi^2)-\frac{1}{2}\left[\frac{\rho'}{\rho}\right]F'\right]u+\tfrac{1}{4}(F')^2=0\ , \end{aligned} \tag{2.14}$$

where u is given by Eq. (2.5), ξ and λ by Eq. (2.10), while F is defined by

$$F=V-\tfrac{1}{2}\left[\frac{\chi''}{\chi}\right]-\lambda=V+\frac{1}{8}\left[\left[\frac{\rho'}{\rho}\right]^2-2\left[\frac{\rho''}{\rho}\right]\right]-\lambda\ . \tag{2.15}$$

An alternative way of writing the two-level density-potential relation is to treat Eq. (2.14) as a quadratic equation in F', which can be solved to yield, with an ambiguity of sign to be resolved through physical boundary constraints,

$$F' = \left[\frac{\rho'}{\rho} u \pm 2u^{1/2}(4F^2 - 4Fu - u^2 - 4\xi^2)^{1/2} \right] . \tag{2.16}$$

If we now insert u from Eq. (2.5) and F from Eq. (2.15) into the right-hand side of Eq. (2.16), we can write an explicit expression for F as $\int^x F'dx$ in terms of only ρ, V, and their derivatives. One can then view Eq. (2.15) as a Schrödinger equation for $\chi = \rho^{1/2}$, to be solved self-consistently for a given V. We will discuss the meaning of this Schrödinger equation in more intuitive terms in Sec. III.

III. DISCUSSION AND SUMMARY

Equation (2.14) is the principal result of the present study. It is worthwhile to relate it to the proposal of one of us[14] that the density should be generated from a Schrödinger equation for $\rho^{1/2} \equiv \chi$ with effective potential energy

$$\mathscr{V}(\mathbf{r}) = V(\mathbf{r}) + V_{\mathrm{Pauli}}(\mathbf{r}) , \tag{3.1}$$

where $V_{\mathrm{Pauli}}(\mathbf{r})$ results from the Fermi statistics. This Pauli potential is essentially, to within an additive constant, the function F introduced through Eq. (2.15). Then Eq. (2.16) can be seen to give, through the quadrature $F = \int^x F'dx$, an expression for V_{Pauli} in the two-level case only in terms of ρ and V and their derivatives.

To see the direct relation of the present treatment to the density-functional Euler equation, we would have, in essence, to solve the ρ-V relation for the potential energy V in terms only of ρ and its derivatives. We have not succeeded in doing this to date. An equivalent procedure would be to get $(\theta')^2$ solely as a function of ρ and its derivatives and then to use Eq. (3.3) for the kinetic energy density. This encounters immediately the cubic equation (2.14) for $u = (\theta')^2$, solved in Appendix A. What is not presently clear to us is whether, if V could be obtained as a functional of ρ, it would merely contain one parameter, which could then be identified with the chemical potential μ of density-functional theory, already appearing in the approximate form (1.1). The present ρ-V relation certainly contains two parameters, λ and ξ, related to the two lowest eigenvalues of standard wave-function theory. Thus, again, we are tempted to speculate that the exact density-functional theory is equivalent to the customary wave-function theory,[15] though no doubt more compact in some sense.

Solution of Eqs. (2.15) and (2.14) self-consistently for given $V(r)$, using, say, a local-density approximation for $V(r)$, or its extension to embody density gradients,[16] and its use in Eq. (1.5) for the Be atom ground-state density will now reflect the "shell structure" of the atomic density; the Pauli potential V_{Pauli}, reflected by F in Eqs. (2.14) and (2.15) resulting from the requirement of Fermi statistics.

Finally, we reiterate that in order to illustrate the relation (2.14) between V and ρ, the linear harmonic oscillator is considered as an example of a model two-level problem in Appendix B.

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APPENDIX A: SOLUTIONS OF CUBIC EQUATION (2.14)

It is of interest to record here the way one can solve the cubic equation (2.14) for u. Writing this in the form

$$u^3 + Bu^2 + Cu + D = 0 , \tag{A1}$$

we evidently have the explicit expressions

$$B = 4F + \tfrac{1}{4}\left[\frac{\rho'}{\rho}\right]^2 , \tag{A2}$$

$$C = 4(F^2 - \xi^2) - \frac{1}{2}\left[\frac{\rho'}{\rho}\right]F' , \tag{A3}$$

and

$$D = \tfrac{1}{4}(F')^2 . \tag{A4}$$

One can, following Cardano, eliminate the quadratic term in Eq (A1) by making the substitution

$$U = u + \frac{B}{3} \tag{A5}$$

to yield

$$U^3 + pU + q = 0 , \tag{A6}$$

where p and q are readily obtained in terms of B, C, and D given above.

The three solutions of Eq. (A6) are then

$$\begin{aligned} U_1 &= 2r\cos\frac{\alpha}{3} , \\ U_2 &= 2r\cos\left[\frac{\alpha}{3} + 120^\circ\right] \\ U_3 &= 2r\cos\left[\frac{\alpha}{3} + 240^\circ\right] , \end{aligned} \tag{A7}$$

where $r = \sqrt{-p/3}$ and $\cos\alpha = -q/2r^3$.

Hence, explicit solutions for u from the cubic equation (2.14) are known.

APPENDIX B: FORM OF THE ρ-V RELATION FOR THE HARMONIC OSCILLATOR

Consider a linear harmonic oscillator with units in which the Hamiltonian H takes the form

$$H=\tfrac{1}{2}p^2+\tfrac{1}{2}x^2\ . \tag{B1}$$

We are dealing here with the first two states occupied:

$$\epsilon_1=\tfrac{1}{2}\ \text{ and }\ \epsilon_2=\tfrac{3}{2}\ . \tag{B2}$$

Hence, from Eq. (2.10)

$$\lambda=1\ \text{ and }\ \xi=-\tfrac{1}{2}\ . \tag{B3}$$

Explicit use of the exact wave functions ϕ_1 and ϕ_2 yields for the density[17]

$$\rho=\pi^{-1/2}\exp(-x^2)Z\ , \tag{B4}$$

where

$$Z=1+2x^2\ . \tag{B5}$$

The resulting expressions for u from Eq. (2.5) and the Pauli potential F from Eq. (2.14) are

$$u=2/Z^2 \tag{B6}$$

and

$$F=(4x^4-3)/(2Z^2)\ . \tag{B7}$$

Finally the explicit form of the ρ-V equation (2.14) is

$$\begin{aligned}u^3+Bu^2+Cu+D\equiv u^3&+[(x^2Z^2-6)/Z^2]u^2\\&-\{[4x^2Z(Z+2)+8(x^2-1)]/Z^4\}u\\&+[4x^2(Z+2)^2/Z^6]=0\ .\end{aligned} \tag{B8}$$

As one can readily verify, this equation is indeed satisfied by u given in Eq. (B6). One way to demonstrate that is to use the Cardano method, described briefly in Appendix A; this leads to the following reduced equation (A6) for U [Eq. (A5)]:

$$\begin{aligned}U^3+pU+q\equiv U^3&-[W/(3Z^2)]U\\&+[2x^2(W+6)/(27Z^2)]=0\ ,\end{aligned} \tag{B9}$$

where $W=x^4Z^2+12$. Since

$$q^2/4+p^3/27=-4(x^4Z^2+8)/(27Z^6)<0\ , \tag{B10}$$

the cubic equation (B9) has indeed three real solutions (A7) defined by

$$r=(-p/3)^{1/2}=3W^{1/2}/Z \tag{B11}$$

and

$$\cos\alpha=-q/(2r^3)=-x^2Z(W+6)/W^{3/2}\ . \tag{B12}$$

Now, from the known solution (B6)

$$U=u+B/3=x^2/3\ . \tag{B13}$$

Hence, from Eq. (A7),

$$\cos\frac{\alpha}{3}=x^2Z/(2W^{1/2})\ ; \tag{B14}$$

this finally yields the expression (B12) via the familiar identity $\cos 3\varphi=4\cos^3\varphi-3\cos\varphi$.

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