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# One-body potential theory in terms of the phase of wave functions for the ground state of the Be atom

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From the work of Slater, which was formally completed by Kohn and Sham, a one-body potential $V(r)$ can be constructed which will generate the ground-state density $n(r)$ of a spherically symmetrical atomic charge cloud. For the case of the Be atom, the 1$s$ and 2$s$ wave functions are written in terms of the density amplitude $[n(r)]^{1/2}$ and a common phase angle $\theta$. It is then shown that $V(r)$ can be characterized solely by this phase angle, and this motivates the setting up of a variational principle only in terms of the phase $\theta$. As an illustration of the method, the Hartree-Fock ground-state density $\rho_{\mathrm{HF}}(r)$ is employed to numerically calculate $\theta_{\mathrm{HF}}(r)$, which is then used to calculate $V_{\mathrm{HF}}(r)$. This provides the practical completion of Slater's proposal for treating exchange for Be. The effect of electron correlation on $V(r)$ is finally estimated using a correlated wave function for Be due to Bunge.

## I. INTRODUCTION

Since the pioneering work of Slater,[1] which was formally completed by Kohn and Sham,[2] the generation of the ground-state density $n(r)$ of an atom or molecule from a carefully constructed one-body potential $V(r)$, into which must be subsumed exchange and correlation interactions, has remained of considerable interest. The present contribution lies in this area, and focuses specifically on the Be atom, following the earlier work of March and Nalewajski.[3] Using a suitably constructed equivalent one-dimensional problem, with $\psi_1 \propto rR_{1s}$, $\psi_2 \propto rR_{2s}$, $r \rightarrow x$, their work is based on writing, following Dawson and March,[4]

$$2^{1/2}\psi_1=\rho^{1/2}\cos\theta \tag{1.1}$$

and

$$2^{1/2}\psi_2=\rho^{1/2}\sin\theta \ , \tag{1.2}$$

with $\rho=\psi_1^2+\psi_1^2$. The normalization and orthogonality conditions on $\psi_1$ and $\psi_2$ then require

$$\int \rho(x)\cos^2\theta \, dx = \int \rho(x)\sin^2\theta \, dx = 2 \tag{1.3}$$

and

$$\int \rho(x)\sin(2\theta)dx = 0 \ . \tag{1.4}$$

What will be demonstrated in the present work is that the problem posed above can, in fact, be formulated solely in terms of the phase $\theta$. The method will then be illustrated by presenting numerical results for the (assumed) underlying potential $V(r)$ starting from the Hartree-Fock ground-state electron density for the Be atom. An estimate of correlation corrections to $V(r)$ is also attempted using the correlated wave function of Bunge.[5]

## II. CHARACTERIZATION OF THE Be-ATOM GROUND STATE BY THE PHASE θ

Following Ref. 3, one has for the relation between electron density $\rho$ and phase $\theta$:

$$\theta''+\frac{\rho'}{\rho}\theta'=2\xi\sin(2\theta) \ , \tag{2.1}$$

where $\xi=(\varepsilon_1-\varepsilon_2)/2$, with $\varepsilon_1$ and $\varepsilon_2$ the eigenvalues corresponding to the wave functions $\psi_1$ and $\psi_2$, respectively, generated by the one-body potential $V$. Equation (2.1), viewed as a first-order differential equation for $\rho$, can be integrated by introducing the function $h(x)$:

$$h(x)=\int^{x}\frac{\sin(2\theta)}{\theta'}dx \ . \tag{2.2}$$

The result is readily verified to be

$$\ln\rho=2\xi h-\ln\theta' \ , \tag{2.3}$$

which may be rewritten as

$$\rho=\frac{1}{\theta'}\exp(2\xi h) \ . \tag{2.4}$$

The integration constant appearing in Eqs. (2.2) and (2.4) can be determined from the normalization condition $\int \rho(x)dx=2$.

The one-body potential can now be expressed solely in terms of $\theta$, by using Eq. (2.8) of Ref. 3. Writing

$$f=\rho'/\rho\equiv[2\xi\sin(2\theta)-\theta'']/\theta' \ ,$$

that result is readily rewritten as

$$V=\tfrac{1}{8}f^2+\tfrac{1}{4}f'+\lambda+\xi\cos(2\theta)-\tfrac{1}{2}(\theta')^2 \ , \tag{2.5}$$

where $\lambda=(\varepsilon_1+\varepsilon_2)/2$.

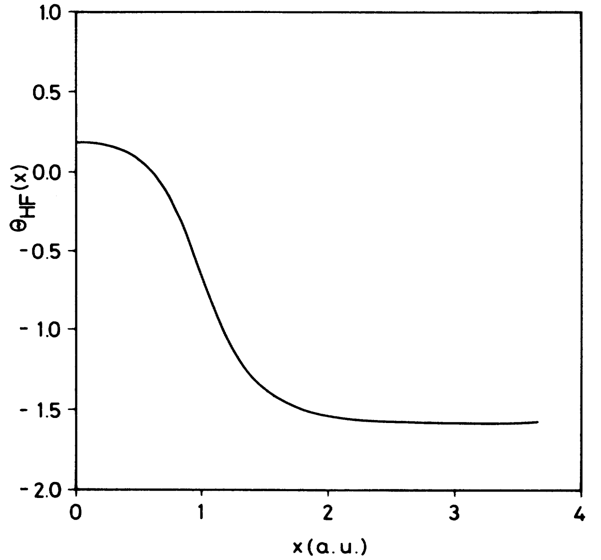

FIG. 1. Hartree-Fock phase $\theta$ for the Be atom.

In the Appendix, Eq. (2.5) is formulated as the Euler equation of an equivalent variational problem. However, for the calculations to be reported below, we merely need note that knowledge of $\rho(x)$ used as input into Eq. (2.1) will allow $\theta(x)$ to be constructed numerically. This, together with the information thereby gained on $\xi$, can be inserted into Eq. (2.5), which allows $V$ to be determined to within the constant $\lambda$.

### III. NUMERICAL RESULTS FOR $V$ VIA PHASE $\Theta$ FOR THE HARTREE-FOCK GROUND-STATE DENSITY OF Be

The above program has been implemented numerically using the approximate representation of Clementi and Roetti[6] of the Hartree-Fock results. Inserting $\rho'/\rho$ using these Hartree-Fock data, Eq. (2.1) was integrated numerically, and results for the phase $\theta_{\mathrm{HF}}(x)$ are plotted in Fig. 1. These data have then been used in Eq. (2.5) to construct the quantity $V_{\mathrm{HF}}(x)-\lambda$ which is displayed in Fig. 2. To within a constant, this completes the program of work started by Slater[1] for the specific, and of course very simple, case of the Be-atom ground state.

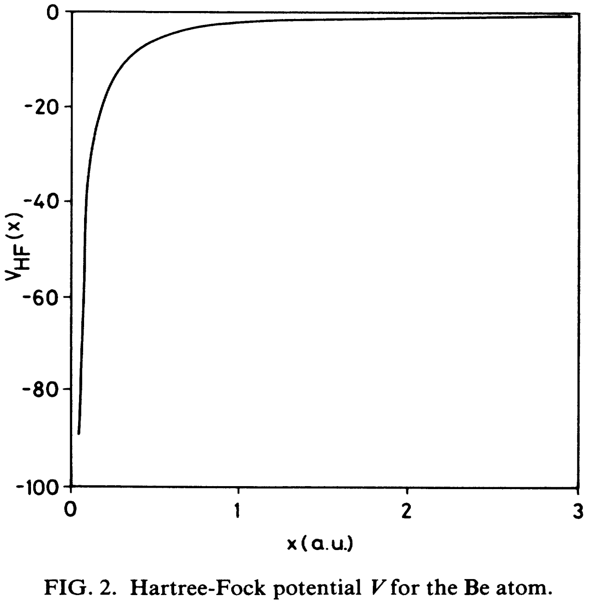

FIG. 2. Hartree-Fock potential $V$ for the Be atom.

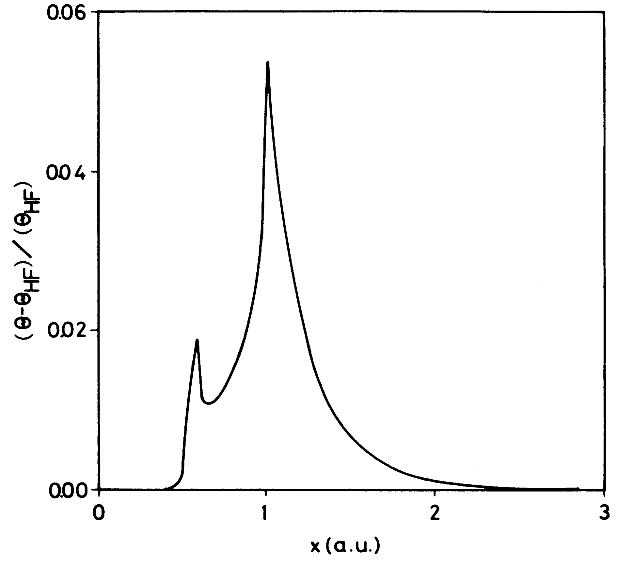

FIG. 3. Shows the relative difference between the Hartree-Fock phase $\theta_{\mathrm{HF}}$ and the phase $\theta$ obtained from the correlated wave function of Bunge (Ref. 5).

### IV. DISCUSSION AND SUMMARY

It seems clear that for Be the exchange contribution to $V(x)$ will dominate the correlation correction. In principle, the correlated wave function of Bunge[5] can be used to construct a $\rho(r)$-transcending Hartree-Fock, which

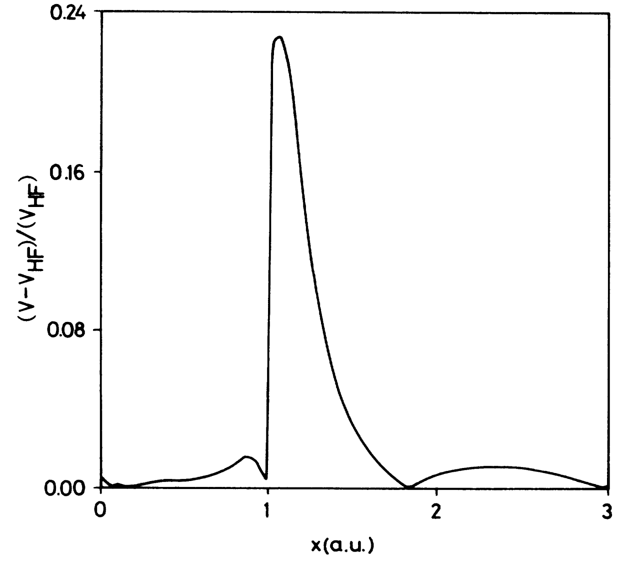

FIG. 4. Shows the relative difference between the Hartree-Fock potential $V_{\mathrm{HF}}$ and the potential $V$ obtained from the correlated wave function of Bunge (Ref. 5).

one can then insert into Eq. (2.1) to construct a slightly refined phase $\theta(x)$. Again $V(x)-\lambda$ can then be calculated from Eq. (2.5).

The relative differences $|\theta-\theta_{\mathrm{HF}}|/|\theta_{\mathrm{HF}}|$ and $|V-V_{\mathrm{HF}}|/|V_{\mathrm{HF}}|$ are plotted in Figs. 3 and 4. The functions $\theta(x)$ and $V(x)$ obtained from the correlated wave function of Bunge are so close to the functions $\theta_{\mathrm{HF}}(x)$ and $V_{\mathrm{HF}}(x)$ that if they were plotted in Figs. 1 and 2 they could not be distinguished from the curves $\theta_{\mathrm{HF}}$ and $V_{\mathrm{HF}}$ with the exception of a small part of the curves. That is why the relative differences $|\theta-\theta_{\mathrm{HF}}|/|\theta_{\mathrm{HF}}|$ and $|V-V_{\mathrm{HF}}|/|V_{\mathrm{HF}}|$ are plotted in Figs. 3 and 4. As the boundary conditions (at $x=0$ and $x\to\infty$) are the same for both $\theta$ and $\theta_{\mathrm{HF}}$, it is obvious that the largest difference between them can be found in the middle. (But the difference is everywhere below 5.3%.) As the potentials $V$ and $V_{\mathrm{HF}}$ have large negative values around $x=0$, the relative difference between them is very small near the nucleus. Having the same asymptotic behavior. $V$ and $V_{\mathrm{HF}}$ are very close together far from the nucleus. As in the middle part of the atom, the absolute value of the potential is rather small; the relative difference between $V$ and $V_{\mathrm{HF}}$ is large.

Nyden and Parr[7] have solved the Hartree-Fock equations for the Be atom using complex one-electron functions. They have obtained integro-differential equations for the density and the phase function $\bar{\theta}$. Their equation for $\bar{\theta}$ is similar to Eq. (2.1); however, the equation for $\bar{\theta}$ contains $n$ instead of $\rho$ and a nonlocal term coming from the Hartree-Fock exchange. Nevertheless, there is only a small difference between $\bar{\theta}$ and $\theta_{\mathrm{HF}}$.[8]

In summary, Eqs. (2.1) and (2.5), and the variational principle constructed in the Appendix, show explicitly how the one-body potential description of the Be ground state, or indeed of any four-electron atomic ion with arbitrary nuclear charge $Z$, can be formulated solely in terms of the phase angle $\theta$.

## APPENDIX: VARIATIONAL PRINCIPLE FOR THE EULER EQUATION RELATING $V$ AND $\theta$

The energy

$$E=T+\int \rho V\,dx=\int \rho(G+V)dx\ , \tag{A1}$$

where

$$G=\tfrac{1}{8}f^2-\tfrac{1}{4}f'+\tfrac{1}{2}(\theta')^2\ . \tag{A2}$$

Taking into account the conditions $\int \phi_i\phi_j=\delta_{ij}$, the Lagrange function of the variational process is

$$\begin{aligned}L=\rho(\theta,\theta')[G(\theta,\theta',\theta'',\theta''')+V-\alpha\cos^2\theta\\ -\beta\sin^2\theta-(\gamma/2)\sin(2\theta)]\ ,\end{aligned} \tag{A3}$$

and thus $L$ is a function of $\theta$, $\theta'$, $\theta''$, and $\theta'''$. Therefore the Euler-Lagrange equation

$$\frac{\partial L}{\partial\theta}-\frac{d}{dx}\frac{\partial L}{\partial\theta'}+\frac{d^2}{dx^2}\frac{\partial L}{\partial\theta''}-\frac{d^3}{dx^3}\frac{\partial L}{\partial\theta'''}=0 \tag{A4}$$

is quite complicated. However, it can be verified to have a solution which is precisely Eq. (2.5).

After a somewhat lengthy differentiation and algebraic manipulation the Euler-Lagrange equation (A4) is given by

$$\begin{aligned}\frac{\rho}{\theta'}\Bigg[&V'+2fV-\frac{1}{4}\frac{\rho'''}{\rho}-2f\xi\cos(2\theta)+4\xi\theta'\sin(2\theta)+f[(\xi-\alpha)\cos^2\theta-(\xi+\beta)\sin^2\theta-(\gamma/2)\sin(2\theta)]\\ &-2\theta'[(2\xi+\beta-\alpha)\sin(2\theta)+\gamma\cos(2\theta)]\Bigg]=0\ ,\end{aligned} \tag{A5}$$

where

$$\rho'''=\rho(f^3+3ff'+f'')\ . \tag{A6}$$

An appropriate choice of the Lagrange multipliers leads to the equation

$$V'+2fV=\frac{1}{4}\frac{\rho'''}{\rho}+2f\xi\cos(2\theta)-4\xi\theta'\sin(2\theta)+2f\lambda\ . \tag{A7}$$

It can be easily seen that the potential $V$ of Eq. (2.5) satisfies Eq. (A7).

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[8] We have subsequently found that Eq. (2.1) is given also by F. E. Harriman, in *Density Functional Theory,* edited by F. Keller and F. L. Gazquez (Springer-Verlag, Berlin, 1983).