Determination of a Wave Function Functional

Xiao-Yin Pan, Viraha Sahni, and Lou Massa
The Graduate School of the City University of New York, New York, New York 10016.

We propose expanding the space of variations in traditional variational calculations for the energy by considering the wave function \( \psi \) to be a functional of a set of functions \( \chi : \psi = \psi(\chi) \), rather than a function. A constrained search in a subspace over all functions \( \chi \) such that the functional \( \psi(\chi) \) satisfies a sum rule or leads to a physical observable is then performed. An upper bound to the energy is subsequently obtained by variational minimization. The rigorous construction of such a constrained-search variational wave function functional is demonstrated.

One of the mostly extensively employed and accurate approximation methods in quantum mechanics is the variational principle for the energy. Consider a quantum mechanical system with Hamiltonian operator \( \hat{H} \). The ground state eigenenergies \( E \) and eigenfunctions \( \Psi \) for this system satisfy the Schrödinger equation \( \hat{H}\Psi = E \Psi \). Next define the functional \( I[\psi] = \int \psi^* \hat{H} \psi \, dr / \int \psi^2 \, dr \). Searching over all bounded, quadratically integrable functions \( \psi \), one obtains \( I[\Psi] = E \), with \( \Psi \) being the solution of the Schrödinger equation associated with energy \( E \). Since \( \delta I[\Psi] = 0 \), the functional \( I[\psi] \) is stationary for \( \psi = \Psi \). In practice, an approximate function \( \psi \) of a particular analytical form is chosen to depend upon a number of variable parameters \( c_i (i = 1, \ldots, p) \). A least upper bound to the ground state energy \( E_0 \) is obtained by solving the \( p \) equations \( \partial I[\psi] / \partial c_i = 0 \), and employing the derived set of values of the parameters \( c_i \) to calculate \( I[\psi] \). In application of the variational principle, however, the space of variations is limited by the choice of form of the function chosen for the approximate wave function. For example, if Gaussian or Slater-type orbitals are employed, then the variational space is limited to such functions. In this paper we propose the idea of overcoming this limitation by expanding the space over which the variations are performed. This then allows for a greater flexibility for the structure of the approximate wave function. We demonstrate the idea of expansion of the variational space by example.

We expand the space of variations by considering the approximate wave function to be a functional of the set of functions \( \chi : \psi = \psi(\chi) \), rather than a function. The space of variations is expanded because the functional \( \psi(\chi) \) can be adjusted through the function \( \chi \) to reproduce any well-behaved function. However, this space of variations is still too large for practical purposes, and so we consider a subset of this space. In addition to the function \( \psi \) being of a particular analytical form and dependent on the variational parameters \( c_i \), the functions \( \chi \) are chosen such that the functional \( \psi(\chi) \) satisfies a constraint. Examples of such constraints on the wave function functional \( \psi(\chi) \) are those of normalization or the satisfaction of the Fermi-Coulomb hole charge sum rule, or the requirement that it lead to observables such as the electron density, the diamagnetic susceptibility, nuclear magnetic constant or any other physical property of interest. A constrained-search over all functions \( \chi \) such that \( \psi(\chi) \) satisfies a particular condition is then performed. With the functional \( \psi(\chi) \) thus determined, the functional \( I[\psi(\chi)] \) is then minimized with respect to the parameters \( c_i \). In this manner both a particular system property of interest as well as the energy are obtained accurately, the latter being a consequence of the variational principle. We refer to this way of determining an approximate wave function as the constrained-search variational method.

As an example of the method we consider its application to the ground state of the Helium atom. In atomic units \( \hbar = m = 1 \), the non-relativistic Hamiltonian is

\[
\hat{H} = (-1/2)\nabla_1^2 - (1/2)\nabla_2^2 - Z/r_1 - Z/r_2 + 1/r_{12},
\]

where \( r_1, r_2 \) are the coordinates of the two electrons, \( r_{12} \) is the distance between them, \( Z = 2 \) is the atomic number. In terms of the Hylleraas coordinates

\[
\begin{align*}
\chi &= \frac{1}{12} \left(1 - \chi(q, s, t, u)\right), \\
\text{with } \Phi(\alpha, s) &= (\alpha^3/\pi)\exp(-\alpha s), \\
\psi(\chi(q, s)) &= \left[1 - \chi(q, s, t, u)(1 + u/2)\right],
\end{align*}
\]

where \( \alpha \) and \( q \) are variational parameters. Any two-electron wave function may be expressed in this most general form.

In our example, we consider \( \chi \) to be a function only of the variable \( s \): \( \psi = \psi(\chi(q, s)) \). Then, this wave function satisfies the electron-electron cusp condition, which in integral form is \( \Psi(r_1, r_2, \ldots, r_N)_{r_1 \rightarrow r_2} = \Psi(r_2, r_2, \ldots, r_N)(1 + \frac{m^2}{2}) + r_1 \cdot C(r_2, r_3, \ldots, r_N) \), where \( r_{12} = r_1 - r_2 \) and \( C(r_2, r_3, \ldots, r_N) \) is an undetermined vector. This is readily seen by Taylor expanding \( \psi(\chi(q, s)) \) about \( u = 0 \). In a similar manner, the wave function \( \psi(\chi(q, s)) \) satisfies the electron-nucleus cusp coalescence condition, which is \( \Psi(r, r_2, \ldots, r_N)_{r \rightarrow 0} = \Psi(0, r_2, \ldots, r_N)(1 - Zr_{12}) + r \cdot A(r_2, r_3, \ldots, r_N) \) with \( A(r_2, r_3, \ldots, r_N) \) being an undetermined vector, for \( \alpha = 2 \). For arbitrary value of the variational parameter \( \alpha \), the electron-nucleus coalescence condition
The Hydrogenic pre-factor $\Phi(\alpha)$ at the value for which the energy is minimized by where $\alpha$
Next consider Eq.(4). If the parameter $\alpha$ were fixed at say the value for which the energy is minimized by the Hydrogenic pre-factor $\Phi(\alpha, s)$, i.e. $\alpha = 27/16$, then there exist many functions $g(s)$ for which the condition of Eq.(4) is satisfied. These solutions correspond to the subspace C as shown in Fig.1.

On the other hand, if the parameter $\alpha$ is variable, then the only way in which the condition of Eq.(4) can be satisfied is if

$$g(s) = 0.$$ (6)

The requirement of Eq.(6) is equivalent to the constrained search over the entire subspace C. Substitution of $f(s, u)$ into Eq.(6) in turn is equivalent to a quadratic equation for the function $\chi(q, s)$:

$$a(q, s)\chi(q, s)^2 + 2b(q, s)\chi(q, s) + c(q, s) = 0,$$ (7)

where

$$a(q, s) = \int_0^s \frac{s^2 u^2 - u^4/3}{(1 + u/2)^2} (1 + qu)^2 e^{-2qu} du,$$ (8)

$$b(q, s) = -\int_0^s \frac{s^2 u^2 - u^4/3}{(1 + u/2)(1 + qu)} [e^{-2qu}(1 + qu) - e^{-qu}] du,$$ (9)

The integrals for the coefficients $a$, $b$, and $c$ are solvable analytically. Solution of the quadratic equation is then equivalent to searching over the entire subspace C. Subspace C is comprised of only two points. These two points corresponding to the two solutions $\chi_1(q, s)$ and $\chi_2(q, s)$ are such that the two wave functions $\psi[\chi_1]$ and $\psi[\chi_2]$ are normalized. Rigorous upper bounds to the ground state energy are then obtained by variational minimization of the functional $I[\psi[\chi]]$ with respect to the parameters $\alpha$ and $q$. The details of the derivation and analytical expressions for the wave function functionals are to be given elsewhere.

The ground state energies obtained from the wave function functionals $\psi[\chi_1]$ and $\psi[\chi_2]$ are given in Table I together with those due to the energy-minimized Hydrogenic pre-factor $\Phi(s)$ with $\alpha = 27/16$, the Hartree-Fock(HF) value,$^{2}$ and the ‘exact’ value of Pekeris.$^{4}$ The functions $\chi_1(q, s)$ and $\chi_2(q, s)$ at the respective energy minimum are plotted in Fig.2. We also quote energy minimized values determined from the wave function functionals $\psi[\chi_3]$ and $\psi[\chi_4]$ obtained by solution of the quadratic equation with $\alpha$ fixed at $\alpha = 27/16$, and $q$ treated as the only variational parameter. (The functions $\chi_3, \chi_4$ differ minimally from those of $\chi_1, \chi_2$.) The satisfaction of the virial theorem and the expectation value of the operator $W = r_1 + r_2$ are also quoted.

We note the following points of interest: (i) The functions $\chi_1(q, s)$, $\chi_2(q, s)$ are very different: $\chi_1(q, s)$ is a positive monotonically decreasing function whereas

![Fig. 1: In the figure, the area of box A represents the space of all normalized square-integrable functions. Functions such as Gaussian or Slater orbitals are represented by lines. The space A is also representative of the functionals $\psi[\chi(s, t, u)]$. The subspace B represents all normalized wave function functionals $\psi[\chi(s, t)]$, and its subspace C that of all normalized functionals $\psi[\chi(s)]$.](image)
\(\chi_2(q,s)\) is a negative monotonically increasing function. They, however, are of about the same magnitude. Thus, the functionals \(\psi[\chi_1]\) and \(\psi[\chi_2]\) are different from each other. Similarly, the functionals \(\psi[\chi_3]\) and \(\psi[\chi_4]\) differ. (ii) In spite of the wave function functionals \(\psi[\chi_1(q,s)]\) and \(\psi[\chi_2(q,s)]\) being different, the corresponding energies are essentially equivalent. (iii) Note that \(E[\chi_2] < E[\chi_1] < E[\chi_4] < E[\chi_3]\). (iv) The improvement in the energies noted in (iii) is also reflected in the two-parameter results in the literature. A 1

Our results demonstrate the advantage of the concept of a wave function functional. (The purpose of the paper is not to determine the most accurate wave function for the He atom ground state.) The energies obtained via the various wave function functionals are to our knowledge the most accurate one- and two-parameter results in the literature. A 1.93% error of the Hydrogenic pre-factor is reduced to errors of 0.45% - 0.43% for the four wave function functionals. The corresponding satisfaction of the virial theorem is 1.61% - 0.08%. As a further point of comparison, we note that our results are superior to those of HF, and the results of \(\psi[\chi_1]\), \(\psi[\chi_2]\) and \(\psi[\chi_4]\) are also superior to a 3-parameter wave function functionals

\(|\psi_s\rangle\) and \(|\psi_s\rangle\) differ. (ii) In spite of the wave function functionals \(\psi[\chi_1(q,s)]\) and \(\psi[\chi_2(q,s)]\) being different, the corresponding energies are essentially equivalent. (iii) Note that \(E[\chi_2] < E[\chi_1] < E[\chi_4] < E[\chi_3]\). (iv) The improvement in the energies noted in (iii) is also reflected in the corresponding satisfaction of the virial theorem. (v) As the constrained search is over the normalized functionals of subspace C, both solutions of the quadratic equation Eq.(7) lead to meaningful energies.

\(\chi_1(q,s)\) and \(\chi_2(q,s)\) .

FIG. 2: The functions \(\chi_1(q,s)\) and \(\chi_2(q,s)\).

As noted above, it is also possible to search over all functions \(\chi(q,s)\) such that the functional \(\psi[\chi]\) leads to a physical property of interest. For example, let us consider the expectation of \(W = r_1 + r_2\):

\(< r_1 + r_2 > = s_0 + \Delta s\). Here \(s_0\) is the expectation from the pre-factor \(\Phi(s)\). Assuming \(\Delta s\) known from experiment or some accurate calculation, and if a wave function functional \(\psi[\chi]\) of the form in the above calculation is employed, then two distinct \(\chi\)'s such that \(< \psi[\chi]|s|\psi[\chi]\> = s_0 + \Delta s\) can be obtained by solution of the quadratic equation

\[a(q,s)\chi(q,s)^2 + b(q,s)\chi(q,s) + [c(q,s) - A] = 0\],

where the constant \(A = 2\Delta s/\alpha^2\), and where the coefficients \(a, b\) and \(c\) are the same as in Eq.(8-10). With the functionals \(\psi[\chi_1]\) and \(\psi[\chi_2]\) thus determined, the energy could then be obtained by minimization of the functional \(I[\psi[\chi]]\) with respect to the parameters \(\alpha\) and \(q\). In this manner, the two wave function functionals would reproduce both the size of the atom exactly and the energy accurately.

For completeness we note that the concept of constrained search in the present work differs from that within density functional theory (DFT). The idea underlying DFT is based on the first Hohenberg-Kohn theorem, according to which the wave function \(\Psi\) is a functional of the ground state density \(\rho(r) : \Psi = \Psi[\rho]\). Thus the energy is a unique functional of \(\rho(r) : E = E[\rho]\). The in principle constrained search within DFT is as follows. One first searches for the infimum of the \(\langle \hat{H} \rangle\)
TABLE I: Rigorous upper bounds to the ground state energy of the Helium atom in (a.u) for different wave functions (WF).
The satisfaction of the virial theorem, and the expectation values of $W = r_1 + r_2$ are also quoted.

| WF    | Parameters       | Energy   | $-V/T < W >$ |
|-------|------------------|----------|--------------|
| $\Phi$ | $\alpha = 1.6875$ | $-2.84766$ | $2.00000$ $1.7778$ |
| $\psi[\chi_1]$ | $\alpha = 1.6875$ $q = 0.581$ | $-2.8804$ | $1.9678$ $1.7778$ |
| $\psi[\chi_1]$ | $\alpha = 1.6875$ $q = 0.180$ | $-2.89061$ | $1.9707$ $1.7778$ |
| $\psi[\chi_1]$ | $\alpha = 1.66414$ $q = 0.5333$ | $-2.89072$ | $1.9973$ $1.8057$ |
| $\psi[\chi_2]$ | $\alpha = 1.6629$ $q = 0.17049$ | $-2.89122$ | $1.9984$ $1.8041$ |

For $HF$, $CK$, and Pekeris, the corresponding energy is a rigorous upper bound to the ground state energy. The satisfaction of the virial theorem, and the expectation values of $W = r_1 + r_2$ are also quoted.

In Q-DFT, the system of electrons is transformed into one of noninteracting fermions such that the same ground state density, energy and ionization potential are obtained. However, in contrast to KS-DFT which is in terms of energy functionals and functional derivatives, the Q-DFT framework involves fields whose quantal sources are expectations of Hermitian operators taken with respect to the wave function. Thus, an approximate wave function functional of the form of Eq. (2) can be employed in this theory with the Slater determinantal pre-factor determined self-consistently. The wave function functional $\psi[\chi = f(\rho)]$ could also be used. Within Q-DFT, the corresponding energy is a rigorous upper bound.

We also mention the work of Colle and Salvetti (CS) who suggested a wave function functional of the density. The CS wave function is similar to Eq. (2) except that the pre-factor is the HF wave function and the correlation term is $f(r_1, r_2) = e^{-\beta^{2}/2} (1 - \chi(R)(1 + r/2))$, with $r = r_1 - r_2$, $R = r_1 + r_2$, $\beta = \rho^{HF}(R)$. CS further assumed that the corresponding Dirac density matrix was that due to the pre-factor. The function $\chi(R)$ was to be determined by requiring that the correction to the HF Dirac density matrix due to the correlation factor $f(r_1, r_2)$ vanishes. Since the HF Dirac density matrix cannot be the same as the exact interacting system density matrix, this is not an exact constraint. Moreover, they did not satisfy this condition, and instead approximated the function $\chi(R)$ by $\chi(R) = \sqrt{\beta}/(1 + \sqrt{\beta})$. A consequence of this was that the resulting wave function was not normalized. There is also no discussion in this work of the general concept of wave function functionals or the idea of constrained search to obtain them.

In conclusion, we have proposed the idea of expanding the space of variations beyond that of standard variational calculations by considering the wave function to be a functional instead of a function, a functional of the functions $\chi$. A constrained search is performed over the functions $\chi$ such that the wave function satisfies a constraint or leads to a physical observable. A rigorous upper bound to the energy is then obtained by variational minimization with respect to any parameters in the wave function functional. The construction of such a constrained-search–variational wave function functional for the ground state of the Helium atom where the search is over the entire requisite subspace is explicitly demonstrated.

This work was supported in part by the Research Foundation of CUNY. L. M. was supported in part by NSF through CREST, and by a “Research Centers in Minority Institutions” award, RR-03037, from the National Center for Research Resources, National Institutes of Health.

---

[1] E. A. Hylleraas, Z. Physik, 48, 469 (1928).
[2] X.-Y. Pan and V. Sahni, J. Chem. Phys. 119, 7083 (2003).
[3] C. F. Fischer, The Hartree-Fock Method For Atoms, John Wiley and Sons, 1977.
[4] C. L. Pekeris, Phys. Rev. 115, 1216 (1959).
[5] S. Caratzoulas and P. J. Knowles, Mol. Phys. 98, 1811 (2000).
[6] J. Goodisman and W. Klemperer, J. Chem. Phys. 38, 721 (1963).
[7] M. Levy, Proc. Natl. Acad. Sci. USA, 76, 6062 (1979); E. H. Lieb, Int. J. Quantum Chem. 24, 243 (1983).
[8] P. Hohenberg and W. Kohn, Phys. Rev. 136B, 864 (1964).
[9] V. Sahni, Quantal Density Functional Theory, Springer Verlag (2004); V. Sahni and X.-Y. Pan, Phys. Rev. Lett. 90, 123001(2003).
[10] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).
[11] R. Colle and O. Salvetti, Theor. Chim. Acta 37, 329 (1975).
[12] R. Singh et al., Phys. Rev. A 60, 4135 (1999).
[13] J. Tao et al., Phys. Rev. A 63, 032513(2001).
