Variational calculation of many-body wave functions and energies from density-functional theory

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A generating coordinate is introduced into the exchange-correlation functional of density-functional theory (DFT). The many-body wave function is represented as a superposition of Kohn-Sham (KS) Slater determinants arising from different values of the generating coordinate. This superposition is used to variationally calculate many-body energies and wave functions from solutions of the KS equation of DFT. The method works for ground and excited states, and does not depend on identifying the KS orbitals and energies with physical ones. Numerical application to the Helium isoelectronic series illustrates the method’s viability and potential.

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Density-functional theory (DFT) is routinely used in quantum chemistry and physics for the calculation of, e.g., ground-state energies and charge distributions. In a typical application of DFT one solves the Kohn-Sham (KS) single-particle equation, with a suitable choice for the exchange-correlation functional, and uses the resulting single-particle orbitals to construct the ground-state particle density. From this density other observables, such as the ground-state energy, can then be calculated. It is well known that the KS Slater determinant is not in itself an approximation to the many-body wave function but only a device for reproducing the correct density. Similarly, the single-particle eigenvalues of the KS equation do not represent the energy spectrum of the system under study, and their differences are not excitation energies. Although excited-state energies and many-body wave functions for both ground and excited states are, in principle, functionals of the ground-state density, they are hard to extract from DFT. For excited-state energies a number of viable methods has been suggested, but these are more complicated than conventional ground-state DFT, and not yet as widely used. Many-body wave functions cannot be calculated at all from standard KS-type calculations.

In the present paper a novel approach based on DFT is proposed, which allows to (i) systematically improve the accuracy of ground-state energies obtained in a standard KS calculation, (ii) calculate excited-state energies, and (iii) obtain variational approximations for the many-body wave functions corresponding to these energies. The device which makes this possible is the Griffin-Hill-Wheeler (GHW) variational method or generator-coordinate method (GCM), which is now briefly described. In the GHW approach one writes the trial wave function \( \Psi \) as an integral transformation of a generating wave function \( \Phi \), according to

\[
\Psi = \int d\alpha f(\alpha)\Phi(\alpha),
\]

where \( \alpha \) is a generating coordinate and the variational principle is applied to the kernel of the integral, \( f(\alpha) \).

The nature of \( \Psi \) and \( \Phi \) (i.e., whether they are many-body or single-body functions) does not matter at this stage, and their coordinate arguments have thus been suppressed. Calculation of the expectation value of the system’s Hamiltonian \( \hat{H} \) with \( \Psi \), followed by variation of the result with respect to \( f(\alpha) \), yields the so-called GHW equation

\[
\int d\alpha' [K(\alpha,\alpha') - ES(\alpha,\alpha')] f(\alpha') = 0. \tag{2}
\]

Here \( K(\alpha,\alpha') = \langle \Phi(\alpha) | \hat{H} | \Phi(\alpha') \rangle \) and \( S(\alpha,\alpha') = \langle \Phi(\alpha) | \Phi(\alpha') \rangle \) are matrix elements of the Hamiltonian with the generator functions \( \Phi(\alpha) \), and the overlap of these functions, respectively. Solution of the GHW equation (2) yields the energies \( E \), which are variational approximations for the eigenvalues of \( \hat{H} \), and the function \( f(\alpha) \) which through (1) determines the corresponding wave functions. The full set of solutions of the eigenvalue problem (2) yields thus the spectrum and wave functions of Hamiltonian \( \hat{H} \).

Originally this method arose in nuclear physics, where \( \Psi \) was taken to be the nuclear many-body wave function, and the generating coordinate \( \alpha \) was interpreted as a ‘deformation parameter’ describing collective oscillations of the nucleus. The generator functions \( \Phi(\alpha) \) were obtained from solving an auxiliary, simplified, Schrödinger equation in which the nuclear potential \( v_\alpha(\mathbf{r}) \) was replaced by a deformed potential \( v_\alpha(\mathbf{r}) \), with \( \alpha \) characterizing the degree of deformation. Outside nuclear physics the GHW approach has been applied to various model Hamiltonians, the electron gas, and molecular electronic-structure calculations, exploring a variety of different choices for the generator functions \( \Phi \) and the generating coordinate \( \alpha \). More recently, it has been used to generate optimized basis functions for Hartree-Fock calculations, starting from a set of simple trial functions. In this type of application \( \alpha \) is iden-
tified with the basis function exponent $\zeta$, and $\Psi$ and $\Phi$ are single-particle functions.

In the present contribution we go back to many-body wave functions. The basic idea is to identify the auxiliary Schrödinger equation with the KS equation of DFT, the deformation potential producing the family of generator functions with the KS potential, and the deformation parameter (or generating coordinate) with a parameter in the exchange-correlation ($xc$) functional. Many functionals, such as the $X\alpha$ and B3-LYP approximations, naturally contain such a parameter, but it can always be introduced by hand in any functional. The present proposal is thus to write the many-body wave function as

$$\Psi(r_1, \ldots r_N) = \int d\alpha f(\alpha) \Phi^{KS}(\alpha; r_1, \ldots r_N), \quad (3)$$

where $\Phi^{KS}(\alpha)$ is the Slater determinant obtained from a KS calculation with $xc$ potential $v_{xc,\alpha}$. Note that the deformation parameter $\alpha$ is neither an adjustable parameter fixed by comparison with experiment nor a variational parameter for a given form of the trial wave function, but rather a generating coordinate that accounts for collective behaviour in $\Psi$ not described by the single-parameter model fixed by comparison with experiment nor a variational parameter $\alpha$ KS calculation with $\Phi$ as

as

$$\Phi^{KS}(\alpha)$$

is the matrix element of the Hamiltonian between single-particle coordinates $r_1, \ldots r_N$ in the Slater determinant $\Phi^{KS}(\alpha; r_1, \ldots r_N)$. Its physical origin is in the deformations of the single-particle potential $v_{xc,\alpha}$, which simulate the collective degrees of freedom of the interacting many-body system.$^6$

The idea proposed here is thus to use DFT potentials and orbitals as input for a GHW calculation, and the GHW Eq. (2) with (3) to gain direct variational access to many-body energies and wave functions. As a first viability test of this scheme it is now applied to the Helium isoelectronic series. For a general two-electron atom in a closed-shell configuration the kernels $K$ and $S$ are evaluated easily. $\Phi^{KS}(\alpha)$ is a $2 \times 2$ Slater determinant formed with one doubly occupied orbital. After performing the sum over spins one is left with only spatial integrals, which need to be calculated numerically, and the kernels take the form $K(\alpha, \alpha') = 2(\alpha|\alpha') (|\alpha + \beta| \alpha') + (\alpha | \beta | \alpha')$, and $S(\alpha, \alpha') = (\alpha | \alpha')^2$, where $|\alpha\rangle$ stands for the KS orbital $\varphi_\alpha(r)$, and $\alpha$ and $\beta$ are the single-particle kinetic and potential energy operators. $\hat{\alpha} = 1/|r - r'|$. Note that the diagonal element ($\alpha = \alpha'$) of the kernel $S$ is simply the energy expression one obtains in a restricted closed-shell Hartree-Fock calculation$^{16}$ for a two-electron atom. A similar formal connection to Hartree-Fock theory will always hold, since $K$ is the matrix element of the Hamiltonian between single Slater determinants. The single-particle orbital $\varphi_\alpha(r)$ is now obtained from a self-consistent KS calculation. For simplicity (and to illustrate an important point below) I choose as $xc$ functional the $X\alpha$ approximation and take as generating coordinate the parameter $\alpha$ present in that functional. (The fact that the GHW generating coordinate and the $X\alpha$ coefficient are both traditionally called $\alpha$ is a coincidence.) The GHW integral equation (2) is then solved by discretization. A suitable mesh for discretizing the integral over $\alpha$ is $\{0, 0.5, 1, 1.5, 2\}$. Five mesh points may appear surprisingly few, but empirically it was found that larger or denser meshes did not significantly change the results.$^{17}$ The calculation thus consists in the following three steps: (i) performing KS $X\alpha$ calculations at the prescribed values of $\alpha$; (ii) using the resulting orbitals to evaluate the kernels $K$ and $S$, according to the above equations; and (iii) discretizing the integral equation (2) on this set of $\alpha$’s and solving it by standard matrix algebra. In the remainder of this paper some representative results obtained in this way are presented.

Table I compares the lowest eigenvalue of Eq. (2) (i.e., our approximation to the many-body ground-state energy) with reference data obtained from numerically exact wave functions.$^{18}$ Considering the simple discretization scheme and generating functional ($X\alpha$), the quantitative agreement achieved is rather surprising. The largest deviation from the reference data is found for Helium, and is only about 1%. Interestingly, this agreement has been obtained by starting out with an $xc$ functional that on its own yields significantly worse energies: the ground-state energy of $He$ calculated from the usual KS scheme, employing the $X\alpha$ functional with the above values of $\alpha$, is found to be $E_{GHW}^{0}=0 = -1.952$ a.u., $E_{GHW}^{0}=0.5 = -2.515$ a.u., $E_{GHW}^{0}=1 = -3.170$ a.u., $E_{GHW}^{0}=1.5 = -3.915$ a.u., and $E_{GHW}^{0}=2 = -4.749$ a.u., respectively, which are all significantly off the true $He$ ground-state energy. Out of these unphysical energies the GHW optimization generates a ground-state energy of $E_{GHW}^{X\alpha}=0 = -2.871$ a.u., which deviates only by about one percent from the exact reference value (see Table I). Since this is a variational calculation it is, of course, rather natural that the GHW energy is better than that obtained with each generating functional (i.e., each value of $\alpha$) individually. GHW opti-

| $X\alpha$ | $E_{GHW}^{X\alpha} - E_{exact}^{0}$ | % deviation |
|----------|---------------------------------|----------|
| $He$     | 2.871                           | 1.1      |
| $Li^+$   | 7.244                           | 0.49     |
| $Be^{2+}$| 13.62                           | 0.29     |
| $B^{3+}$ | 22.00                           | 0.14     |
| $C^{4+}$ | 32.37                           | 0.12     |
| $N^{5+}$ | 44.75                           | 0.067    |
| $O^{6+}$ | 59.12                           | 0.068    |
| $F^{7+}$ | 75.50                           | 0.040    |
mization can thus be used to systematically improve on results obtained from a given input density functional, which need not be very good on its own. On the other hand, the $X\alpha$ GHW value $-2.871\text{a.u.}$, found above, is also closer to the exact result $E_{\text{exact}}^{X\alpha} = -2.904\text{a.u.}$ than the ones obtained with Hartree-Fock ($E_{\text{HF}}^{X\alpha} = -2.862\text{a.u.}$) or LDA ($E_{\text{DFT}}^{X\alpha} = -2.835\text{a.u.}$). This improvement may appear surprising because the $X\alpha$ functional in itself can be interpreted as a rather simple approximation to both Hartree-Fock and LDA, but is simply explained by noting that in the present context the approximation to both Hartree-Fock and LDA, but is simply explained by noting that in the present context the $X\alpha$ functional (or any other generator functional from DFT that could be used instead) only serves as a convenient way to build a family of continuously parametrized generator determinants $\Phi(\alpha)$, and is not used directly to obtain the desired results.

In principle, the $N$ eigenvalues of the GHW equation found by discretizing it as an $N \times N$ matrix equation provide the $N$ lowest-lying energies of the original Hamiltonian, but the quality of the resulting energies will depend on the nature of the generator functions. The present calculation takes ground-state KS determinants to form the generator function and thus does not directly aim at excited states. However, from the second-lowest eigenvalue of the GHW equation one obtains an estimate for the energy of the lowest excited state with same symmetry as the ground state. For $\text{He}$ this is the $2^1S_0$ para state, with an energy of $-2.146\text{a.u.}$ The value found in the above ground-state GHW calculation is $E_{\text{GHW}}^{X\alpha} = -1.788\text{a.u.}$ and deviates from this by 16.7%. A ground-state GHW-DFT calculation thus allows one to obtain estimates of the energies of excited states with the same symmetry as the ground state. It is thus complementary to methods based on minimization in symmetry subspaces, which give access to excited states of symmetry different from the ground state. Calculations optimized for specific target excited states, using excited-state KS Slater determinants as generator functions instead of ground-state ones, are expected to provide better results for the corresponding excitation energies.

Another interesting application of GHW variational optimization in DFT is the calculation of many-body wave functions. Within the GHW scheme the many-body wave function $\Psi$ is known in terms of the family of generator functions $\Phi(\alpha)$ and the weight function $f(\alpha)$, by means of Eq. (1). After discretization, the weight function reduces to a set of coefficients $f(\alpha)$, which can be read off directly from the components of the eigenvector corresponding to a given eigenvalue $E$ of Eq. (2). These coefficients are thus automatically obtained together with the eigenvalues. As an explicit example, the (unnormalized) many-body wave function obtained together with the above result of $E_{\text{GHW}} = -2.871\text{a.u.}$ for the $\text{He}$ ground state is

\[ \Psi_{\text{He}}^{X\alpha} = -0.0529\Phi^{KS}_{\alpha=0} + 0.276\Phi^{KS}_{\alpha=0.5} - 0.451\Phi^{KS}_{\alpha=1} + 0.770\Phi^{KS}_{\alpha=1.5} - 0.354\Phi^{KS}_{\alpha=2}, \tag{4} \]

while the one obtained together with $E_{\text{GHW}}^{\text{He}} = -59.12\text{a.u.}$ for the $O^{6+}$ ground state is

\[ \Psi_{\text{He}^{6+}}^{\text{x}} = -0.116\Phi^{KS}_{\alpha=0} + 0.539\Phi^{KS}_{\alpha=0.5} - 0.786\Phi^{KS}_{\alpha=1} + 0.279\Phi^{KS}_{\alpha=1.5} + 0.0263\Phi^{KS}_{\alpha=2}, \tag{5} \]

where the $\Phi^{KS}(\alpha)$ are the KS Slater determinants obtained in the generator $X\alpha$ calculations for $\text{He}$ and $O^{6+}$, respectively. Wave functions for excited states are obtained in just the same way from the components of the higher eigenvectors.

In a variational calculation, such as the one performed here, energies are typically obtained with higher accuracy than wave functions. However, the simple five-term expansions, given above, already suffice to obtain expectation values of observables that are comparable to those obtained with other methods. As an example, consider the expectation value $\langle \Psi_0 | r^n | \Psi_0 \rangle$, for $n$ ranging from $-2$ to $+2$. Results for the $\text{He}$ atom, calculated with the GHW wave function (4) are listed in Table II. In spite of the simplicity of the $X\alpha$ functional and the inferiority of variational wave functions to variational energies, the expectation values obtained with the five-term GHW-optimized $X\alpha$ wave function are found to be close to those obtained from a much more sophisticated density functional.

**Table II:** Expectation value of the operator $r^n$ for various values of $n$ calculated with the Helium GHW many-body wave function (4), compared with results from a standard DFT calculation using the B88-LYP functional\(^{19,20}\) (in a.u., and after normalization).

| $n$ | $\langle r^n \rangle_{\text{GHW} - X\alpha - \text{DFT}}$ | $\langle r^n \rangle_{\text{B88-LYP} - \text{DFT}}$ |
|-----|---------------------------------|---------------------------------|
| -2  | 5.74                           | 5.98                           |
| -1  | 1.66                           | 1.69                           |
| 0   | 1.00                           | 1.00                           |
| 1   | 0.928                          | 0.964                          |
| 2   | 1.16                           | 1.26                           |

Expressions (4) and (5) for $\Psi_0$ also allow us to see clearly the difference between the present scheme and configuration interaction (CI). In CI $\Psi_0$ is written as a linear combination of Slater determinants that all stem from the same HF calculation. Individual determinants differ by systematically substituting occupied single-particle orbitals by unoccupied ones. In the present scheme $\Psi_0$ is also a linear combination of Slater determinants, but each determinant comes from a different KS calculation, the amount and nature of the difference being specified by the deformation coordinate $\alpha$. The determinants in the present expansion thus stem from Hamiltonians with different potentials. This implies that each of them can be interpreted as an effective resummation of a large number of CI-type determinants arising from a fixed Hamiltonian. Another consequence is that the individual determinants in the GHW expansion are not mutually orthogonal. Interestingly, representation
many-body wave functions in terms of non-orthogonal determinants has previously been shown, in the context of the resonating Hartree-Fock method, to be an efficient way to account for strong Coulomb correlations not readily accounted for by traditional expansions.\textsuperscript{21,22,23}

In summary, the present paper proposes to combine two many-body methods (DFT and GHW), each of which is successful in its field of origin (electronic-structure theory and nuclear physics, respectively), but which had not previously been brought to work together. At the heart of the present proposal is Eq. (3), which expresses the many-body wave function as a weighted superposition of Kohn-Sham determinants, each arising from a differently deformed exchange-correlation potential. As a first viability test the method has been applied to the He isoelectronic series. A full judgement of the powers of GHW-DFT must await systematic tests for a wide variety of physical systems and generator functionals, but the present initial exploration shows that (i) ground-state energies can be obtained that are considerably better than those calculated from both the generator functional and more sophisticated methods approximated by it, (ii) many-body wave functions are obtained with almost no additional numerical effort, and yield expectation values that are close to those given by other methods, and (iii) access to excited state energies and wave functions is, in principle, possible, too.

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