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Generalization of the optimized-effective-potential model to include electron correlation: A variational derivation of the Sham-Schlüter equation for the exact exchange-correlation potential

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The now classic optimized-effective-potential (OEP) approach of Sharp and Horton, [Phys. Rev. **90**, 317 (1953)] and Talman and Shadwick [Phys. Rev. A **14**, 36 (1976)] seeks the local potential that is variationally optimized to best approximate the Hartree-Fock exchange operator. The resulting OEP can be identified as the exchange potential of Kohn-Sham density-functional theory. The present work generalizes this OEP approach to treat the correlated case, and shows that the Kohn-Sham exchange-correlation potential is the variationally best local approximation to the exchange-correlation self-energy. This provides a variational derivation of the equation for the exact exchange-correlation potential that was derived by Sham and Schlüter using a density condition. Implications for an approximate physical interpretation of the Kohn-Sham orbitals are discussed. A correlated generalization of the Sharp-Horton–Krieger-Li-Iafrate [Phys. Lett. A **146**, 256 (1990)] approximation of the exchange potential is introduced in the quasiparticle limit.

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I. INTRODUCTION

The exchange-correlation potential plays a central role in Kohn-Sham density-functional theory (DFT). Thus different formal approaches to the derivation of an exact expression for the exchange-correlation potential, v_{xc}, are useful for the insight they provide into the nature and interpretation of v_{xc}. The present work generalizes the Hartree-Fock optimized-effective-potential (OEP) approach of Sharp and Horton [1] and Talman and Shadwick [2] to treat the correlated case, and yields a variational derivation of the Sham-Schlüter equation for the exact exchange-correlation potential.

Sham and Schlüter [3] derived an expression for the exact exchange-correlation potential which is based directly on the definition of the Kohn-Sham v_{xc} as the unique local potential whose orbital charge densities sum to the true total charge density. This translates into a *density condition* which can be written in the many-body Green function formalism[1] as

$$\begin{aligned} 0 &= n(\mathbf{r}) - n_{\text{KS}}(\mathbf{r}) \\ &= \sum_{\sigma} \frac{1}{2\pi i} \oint_U \left[G(\mathbf{r}\sigma,\mathbf{r}\sigma;\omega) - G_{\text{KS}}(\mathbf{r}\sigma,\mathbf{r}\sigma;\omega)\right] d\omega, \quad (1.1) \end{aligned}$$

where U denotes a counterclockwise contour about the upper half complex plane, and all equations are expressed in Hartree atomic units. Since the true Green function is related to the Kohn-Sham Green function by the Dyson equation

$$\hat{G}(\omega) = \hat{G}_{\text{KS}}(\omega) + \hat{G}_{\text{KS}}(\omega)\left[\hat{\Sigma}^{\text{xc}}(\omega) - v_{\text{xc}}^{\text{KS}}\right]\hat{G}(\omega)\,, \quad (1.2)$$

Eq. (1.1) becomes what will be referred to as the Sham–Schlüter equation,

$$\begin{aligned} 0 = \Delta n(\mathbf{r}_1) = \sum_{\sigma_1} \frac{1}{2\pi i} \oint_U \int\int & G_{\text{KS}}(\mathbf{r}_1\sigma_1,2;\omega) \\ & \times\{[\Sigma^{\text{xc}}(2,3;\omega;G] - v_{\text{xc}}^{\text{KS}}(\mathbf{r}_2)\delta(2-3)\} \\ & \times G(3,\mathbf{r}_1\sigma_1;\omega)\, d2d3d\omega\,, \quad (1.3) \end{aligned}$$

where the spin-orbital notation $i \equiv (\mathbf{r}_i,\sigma_i)$ has been introduced and the notation has been chosen to emphasize that the exchange-correlation self-energy $\hat{\Sigma}^{\text{xc}}(\omega;G]$ may be regarded as a functional of the true Green function.[2] Writing the Kohn-Sham Green function as

$$\hat{G}_{\text{KS}}(\omega) = \{\omega\hat{1} - (\hat{h}_H[n] + \hat{v}_{\text{xc}}^{\text{KS}}[n])\}^{-1}\,, \quad (1.4)$$

where $\hat{h}_H[n]$ is the Hartree Hamiltonian, the Sham-Schlüter equation becomes a nonlinear equation for the "exact" Kohn-Sham exchange-correlation potential cor-

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[1] The reader is assumed to be familiar with the formalism of density-functional theory and many-body Green functions. Good reviews of density-functional theory can be found in Refs. [4,5]. The Green function method is described in a number of texts [6,7] and review articles [8–10] on many-body theory; Refs. [11,12] provide a connection with wave function theory.

[2] In the notation used here, functionals are distinguished from functions by the use of square brackets. Thus F[f] is a functional of f, F(x) is a function of x, and F(x; f] is both a function of x and a functional of f.

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responding to whatever exchange-correlation approximation is used in constructing the self-energy. Since the complex pole structure of Green functions for interacting systems makes the exact Sham-Schlüter equation (1.3) very difficult to solve, it is generally approximated by replacing the true Green function with the Kohn-Sham Green function to obtain the "linear response Sham-Schlüter equation,"

$$0 = \delta n(\mathbf{r}_1) = \sum_{\sigma_1} \frac{1}{2\pi i} \oint_{\mathcal{U}} \int \int G_{\mathrm{KS}}(\mathbf{r}_1\sigma_1, 2; \omega) \left\{ \Sigma^{\mathrm{xc}}(2,3;\omega; G_{\mathrm{KS}}] - v_{\mathrm{xc}}^{\mathrm{KS}}(\mathbf{r}_2)\delta(2-3) \right\} G_{KS}(3, \mathbf{r}_1\sigma_1; \omega)\, d2d3d\omega \,, \tag{1.5}$$

which is again a nonlinear equation for $v_{\mathrm{xc}}^{\mathrm{KS}}$. Note that this equation states that the first-order response of (rather than the total change in) the charge density to the perturbation converting the Kohn-Sham equation into Dyson's quasiparticle equation,

$$\hat{h}_H[n_{\mathrm{KS}}] + \hat{v}_{\mathrm{xc}}^{\mathrm{KS}}[n_{\mathrm{KS}}] \to \hat{h}_H[n_{\mathrm{KS}}] + \hat{\Sigma}^{\mathrm{xc}}(\omega; G_{\mathrm{KS}}], \tag{1.6}$$

is zero, which appears to be an excellent approximation, though a more detailed investigation of this approximation would be desirable.

An alternative approach, also based upon the charge density condition, was given by Sham [13] who, after deriving a perturbative expression for the exact exchange-correlation energy, used a functional derivative identity to rederive the Sham-Schlüter equation [Eq. (1.3)] from his expression for the exchange-correlation energy. It is interesting to note that the functional derivative identity used by Sham is similar to one which will be used here. However, the present work is based on a variational approach whereas Sham uses the density condition and does not variationally optimize the energy.

In the exchange-only case, the linear response Sham-Schlüter equation has been derived variationally, via the optimized-effective-potential approach. In contrast to the approaches of Sham and Schlüter [3] and of Sham [13] which are aimed at constructing the exact v_{xc} of Kohn-Sham theory from the equality of the densities of the interacting and noninteracting systems, the OEP approach traces its origin to Slater's initial concept [14] of v_x as a local approximation to the nonlocal exchange operator in the Hartree-Fock approximation. Thus the classic OEP problem of Sharp and Horton [1] and Talman and Shadwick [2] seeks the energy-independent local potential whose orbitals minimize the Hartree-Fock (HF) energy expression. As is well known, the HF equations are the result of applying the Rayleigh-Ritz variational principle with the constraint that the many-electron trial wave function has the form of a single Slater determinant. The HF OEP problem simply takes this one step further by introducing the additional constraint that the orbitals used to construct the Slater determinant are all eigenfunctions of an orbital Hamiltonian with an *energy-independent, local potential.* Lifting this constraint gives back the eigenfunctions of the true HF orbital Hamiltonian. Hence the OEP ($v_{\mathrm{x}}^{\mathrm{OEP}}$) constitutes the variationally best local approximation for the nonlocal HF exchange operator ($\hat{\Sigma}^{\mathrm{x}}$). The density condition defining the Kohn-Sham potential is not used in this approach. So there is no *a priori* connection between $v_{\mathrm{x}}^{\mathrm{OEP}}$ and the Kohn-Sham v_x^{KS}. However, the HF OEP equation obtained from this procedure is identical to the linear response Sham–Schlüter equation for the exact Kohn-Sham exchange potential v_x^{KS} [13], so v_x^{OEP} may be identified with the exact (exchange-only) Kohn-Sham potential v_x^{KS}. Thus v_x^{KS} can be interpreted as the variationally best local approximation to $\hat{\Sigma}^x$. This analysis has been limited to the exchange-only case for lack of an OEP treatment capable of handling the general correlated case.

A few extensions of the OEP approach have been made which allow the treatment of correlation in a limited way. Aashamar, Luke, and Talman [15,16] gave a partial OEP treatment at the multiconfigurational self-consistent field (MCSCF) level. Their method involves two steps which must be iterated to self-consistency. The first step is a small configuration-interaction (CI) calculation used to determine the coefficients entering into the linear combination of Slater determinants. The second step is an orbital optimization at fixed CI coefficients. The treatment of correlation becomes complete only in the limit of a full CI expansion. Yet only the orbital optimization step is amenable to the OEP procedure, and it yields a CI-coefficient-dependent local exchange-correlation potential. Furthermore, it is difficult to relate this MCSCF OEP to Kohn and Sham's v_{xc}, given the single determinental nature of Kohn-Sham DFT. Aashamar, Luke, and Talman have also introduced orbital angular-momentum-dependent OEP's, but these are clearly distinct from the Kohn-Sham v_{xc}, which is an orbital-independent potential. The second extension of the OEP approach to include some correlation is that of Norman and Koelling [17] and Li, Krieger, Norman, and Iafrate [18] who applied the OEP approach to the energy expression for the self-interaction corrected (SIC) local density approximation (LDA). The SIC-LDA method improves on the Kohn-Sham LDA method by removing self-interaction errors, but in so doing departs from Kohn-Sham theory by introducing an orbital-dependent exchange-correlation potential. The OEP approach corrects this "problem" by finding the best corresponding orbital-independent Kohn-Sham exchange-correlation potential. Exchange and correlation are, of course, treated at no better than the SIC-LDA level by this method. Thus neither the MCSCF nor the SIC-LDA OEP approach is able to deal with electron correlation effects in a general fashion.

In the present work, the OEP approach is extended to treat the correlated case in a general way. This is done by starting with an exact, variational energy expression [19,20], $E[G; G_0]$, which is a functional of the fully dressed Green function G and of the reference Green function G_0, and whose associated variational principle yields the Dyson equation. Such an energy expression arises naturally when resummations are used in a self-consistent formulation of many-body perturbation theory. This is the same energy expression that was used by Sham [13] in his derivation of an exact expression for E_{xc}. However, the present work takes a variational approach, based on the variational principle associated with Klein's energy expression. This use of the Green function formalism allows the development of the exchange-correlation OEP, $v_{\mathrm{xc}}^{\mathrm{OEP}}$, to parallel the exchange-only treatment in a natural way. The exchange-correlation OEP problem defined here simply seeks the potential which is local in both space and time and whose Green function makes the energy $E[G;G_0]$ stationary. This is analogous to the Sharp and Horton [1] and Talman and Shadwick [2] approach and equivalent to their classic OEP procedure in the exchange-only case. However, in the exchange-correlation case, the $v_{\mathrm{xc}}^{\mathrm{OEP}}$ so produced is now the variationally best local approximation to the full exchange-correlation self-energy $\hat{\Sigma}^{\mathrm{xc}}(\omega)$. It will be seen that this OEP equation is identical to the linear response Sham-Schlüter equation for the exact $v_{\mathrm{xc}}^{\mathrm{KS}}$. Thus v_{xc} can now be interpreted as the variationally best local approximation to the exchange-correlation self-energy, $\hat{\Sigma}^{\mathrm{xc}}(\omega)$, nicely analogous to the earlier statement about v_x. This is done in Sec. II. The problem of a spatially nonlocal, but temporally local, optimized effective potential is considered briefly in the conclusion. The quasiparticle limit and the average energy approximation are considered in Sec. III, in order to give further insight into the relation between v_{xc} and v_x, and to give the correlated analogs of the approximations of Slater [14] and of Krieger, Li, and Iafrate [21,22].

Finally, the present work, taken together with the Sham-Schlüter equation for the exact Kohn-Sham v_{xc}, can be regarded (within the linear response approximation to the Sham-Schlüter equation), as providing an alternative derivation of the Kohn-Sham equation, as the variationally best local approximation to Dyson's quasiparticle equation. This is interesting from the point of view of an approximate physical interpretation of the Kohn-Sham orbitals, and is discussed in the conclusion.

II. OPTIMIZED EFFECTIVE POTENTIAL

A. Energy functional

Klein [20] showed that a certain form of Green function self-energy expansion permits the formulation of a variational energy functional of the Green function. Essentially the same result was also given by Luttinger and Ward within a finite temperature formalism [19]. When the exact self-energy is cast in this form, the exact Green function is recovered from this procedure. However, given that the exact self-energies are known for very few systems, the fact that it is applicable to approximate forms is also important. A brief summary of Klein's result is given here since it is fundamental to the present work.

When the self-energy is expanded as a series in powers of the electron repulsion and zero-order Green function, many self-energy diagrams are seen to include "self-energy insertions" which may be removed by a resummation procedure which consists of replacing the zero-order Green function by the true Green function in the series expression for the self-energy. The result is a self-consistent self-energy, $\hat{M}(\omega;G]$, which is a sum of "skeleton diagrams." This procedure is quite general and may be applied, for example, to a self-energy described by Hedin's GW [Green function (G) times screened interaction (W) approximation] [23] as well as to the exact self-energy. Klein [20] has used the special properties of such a self-energy to show that the total (electronic) energy can be written (in present notation) in the form

$$E[G;G_0] = \frac{1}{2\pi i}\oint_U \omega \mathrm{tr} G_0(\omega)\,d\omega + \sum_{m=1}^{\infty}\frac{1}{2m}\left\{\frac{1}{2\pi i}\oint_U \mathrm{tr}\{M^{(m)}(\omega;G]G(\omega)\}\,d\omega\right\} - \frac{1}{2\pi i}\oint_U \mathrm{tr}\left\{G_0^{-1}(\omega)G(\omega) + \ln\left[G_0(\omega)G^{-1}(\omega)\right]\right\}\,d\omega\,, \tag{2.1}$$

where the trace denotes an integral over spatial coordinates and a summation over spin coordinates and $M^{(m)}(\omega;G]$ is the part of the self-energy involving m explicit electron repulsions (i.e., not counting electron repulsion contributions which enter implicitly through G). Then the functional derivative

$$\frac{\delta E[G;G_0]}{\delta G(1,2;\omega)} = \frac{e^{i\eta\omega}}{2\pi i}\left\{M(2,1;\omega;G] - G_0^{-1}(2,1;\omega) + G^{-1}(2,1;\omega)\right\}, \tag{2.2}$$

where $\eta = 0^+$, so the variational condition,

$$\frac{\delta E[G;G_0]}{\delta G(1,2;\omega)} = 0\,, \tag{2.3}$$

gives Dyson's equation and hence the "true" Green function corresponding to the (possibly truncated) sum of skeleton diagrams used in constructing the self-energy. Klein notes that his variational principle gives a stationary point but not necessarily a minimum. For completeness, note also that in general there is no global stationary point for the double functional, $E[G;G_0]$, since

$$\frac{\delta E[G;G_0]}{\delta G_0(1,2;\omega)} = \frac{e^{i\eta\omega}}{2\pi i}\left[\omega\delta(2-1) - (G_0^{-1}GG_0^{-1})(2,1;\omega) + G_0^{-1}(2,1;\omega)\right] \tag{2.4}$$

is not generally zero when $\delta E[G;G_0]/\delta G = 0$.

Sham [13] used this same energy expression (2.1) to give an expression for the exact exchange-correlation energy, E_{xc}, and its functional derivative, v_{xc}. In the present work, this energy expression is used in a different way, taking advantage of its associated variational principle.

B. Optimized effective potential

Consider now the problem of finding the optimized effective exchange-correlation potential. By definition, the OEP is a local potential $v_{\mathrm{xc}}^{\mathrm{OEP}}(\mathbf{r})$, where "local" means simultaneously local in time,

$$v_{\mathrm{xc}}^{\mathrm{OEP}}(1t_1,2t_2)=v_{\mathrm{xc}}^{\mathrm{OEP}}(1,2)\delta(t_1-t_2)\,, \tag{2.5}$$

and local in space,

$$v_{\mathrm{xc}}^{\mathrm{OEP}}(1,2)=v_{\mathrm{xc}}^{\mathrm{OEP}}(\mathbf{r}_1)\delta(1-2)\,, \tag{2.6}$$

which is optimized according to a given variational principle. Klein's variational principle will be used, and the constraints enter through the Green function.

In the exchange-only case, there is no nonlocality in time to start with, so the only constraint is that of replacing the nonlocal Hartree-Fock exchange operator in the HF Green function expression with a potential which is local in space. In the correlated case, the constraint that $v_{\mathrm{xc}}^{\mathrm{OEP}}(\mathbf{r})$ be local in time (equivalently, that it be energy independent in the energy representation) makes the OEP Green function an independent-particle Green function,

$$\hat{G}_{\mathrm{OEP}}(\omega)=\{\omega\hat{1}-(\hat{h}_H[n_{\mathrm{OEP}}]+\hat{v}_{\mathrm{xc}}^{\mathrm{OEP}})\}^{-1}\,. \tag{2.7}$$

Here, it should be recalled that $\hat{h}_H[n_{\mathrm{OEP}}]$ designates the Hartree Hamiltonian constructed with the OEP charge density, obtained from G_{OEP} via

$$\begin{aligned}n_{\mathrm{OEP}}(\mathbf{r})&=\sum_{\sigma}\frac{1}{2\pi i}\oint_{\mathcal{U}}G_{\mathrm{OEP}}(\mathbf{r}\sigma,\mathbf{r}\sigma;\omega)\,d\omega\\&=\sum_{\sigma}\sum_{i}^{\mathrm{occupied}}\psi_i^{\mathrm{OEP}}(\mathbf{r}\sigma)\psi_i^{\mathrm{OEP}*}(\mathbf{r}\sigma)\,.\end{aligned} \tag{2.8}$$

The quasiparticle equation corresponding to the OEP Green function is

$$\{\hat{h}_H[n_{\mathrm{OEP}}]+\hat{v}_{\mathrm{xc}}^{\mathrm{OEP}}\}\psi_r^{\mathrm{OEP}}=\epsilon_r^{\mathrm{OEP}}\psi_r^{\mathrm{OEP}}\,. \tag{2.9}$$

This serves to define the OEP orbitals and OEP orbital energies.

Finding the OEP for Klein's variational principle consists of finding the local potential $v_{\mathrm{xc}}^{\mathrm{OEP}}(\mathbf{r})$ whose Green function G_{OEP} makes Klein's energy expression stationary. That is,

$$\frac{\delta E_{\mathrm{OEP}}[G_{\mathrm{OEP}};G_0]}{\delta v_{\mathrm{xc}}^{\mathrm{OEP}}(\mathbf{r})}=0\,. \tag{2.10}$$

This is equivalent to finding the stationary point of the energy with respect to variations in the Green function, subject to the constraint that the Green function have the form (2.7) (i.e., that $v_{\mathrm{xc}}^{\mathrm{OEP}}$ be local).

The energy expression can be simplified somewhat because the fact that the OEP Green function is an independent-particle Green function means that it may also be used as the reference Green function G_0 in $E[G_{\mathrm{OEP}};G_0]$, with the result that the last integral in Eq. (2.1) vanishes. The OEP energy expression then takes the form of a perturbative estimate $E[G_{\mathrm{OEP}};G_{\mathrm{OEP}}]$ of the exact energy,

$$\begin{aligned}E_{\mathrm{OEP}}[G_{\mathrm{OEP}}]&\equiv E[G_{\mathrm{OEP}};G_{\mathrm{OEP}}]\\&=\frac{1}{2\pi i}\oint_{\mathcal{U}}\omega\mathrm{tr}G_{\mathrm{OEP}}(\omega)\,d\omega+\sum_{m=1}^{\infty}\frac{1}{2m}\left\{\frac{1}{2\pi i}\oint_{\mathcal{U}}\mathrm{tr}\{M^{(m)}(\omega;G_{\mathrm{OEP}}]G_{\mathrm{OEP}}(\omega)\}\,d\omega\right\}\,.\end{aligned} \tag{2.11}$$

When the contour integrals are evaluated and explicit forms are used for the self-energy contributions, the OEP energy expression differs from the Møller-Plesset [24] energy expression, familiar in molecular calculations, only in that (1) OEP orbitals and orbital energies are used in the OEP energy expression instead of the Hartree-Fock orbitals and energies used in Møller-Plesset theory, and (2) in the Møller-Plesset energy expression, terms of third and higher order contain self-energy insertions which are absent in the OEP energy expression. These self-energy insertions disappear naturally when infinite-order resummations are carried out and the *exact* Dyson orbitals and orbital energies are introduced as in Klein's expression. Writing terms explicitly to second order,

$$\begin{aligned}E_{\mathrm{OEP}}=&-\frac{1}{2}\sum_{i=1}^{N}\langle\psi_i^{\mathrm{OEP}}|\nabla^2|\psi_i^{\mathrm{OEP}}\rangle+\int v(\mathbf{r})n_{\mathrm{OEP}}(\mathbf{r})\,d\mathbf{r}+\frac{1}{2}\int\int\frac{n_{\mathrm{OEP}}(\mathbf{r}_1)n_{\mathrm{OEP}}(\mathbf{r}_2)}{r_{12}}\,d\mathbf{r}_1d\mathbf{r}_2\\&-\frac{1}{2}\int\int\frac{|\gamma_{\mathrm{OEP}}(1,2)|^2}{r_{12}}\,d1d2+\frac{1}{4}\sum_{i,j,a,b}\frac{|\langle\psi_i^{\mathrm{OEP}}\psi_j^{\mathrm{OEP}}|1/r_{12}|\psi_a^{\mathrm{OEP}}\psi_b^{\mathrm{OEP}}\rangle|^2}{\epsilon_i^{\mathrm{OEP}}+\epsilon_j^{\mathrm{OEP}}-\epsilon_a^{\mathrm{OEP}}-\epsilon_b^{\mathrm{OEP}}}+\cdots\,,\end{aligned} \tag{2.12}$$

where it is convenient here and throughout to use the orbital index convention,

$$\underbrace{a\,b\,c\cdots f\,g\,h}_{\mathrm{unoccupied}}\;\underbrace{i\,j\,k\,l\,m\,n}_{\mathrm{occupied}}\;\underbrace{o\,p\,q\cdots x\,y\,z}_{\mathrm{either}}\,, \tag{2.13}$$

and the integral is between two-electron Slater determinants,

$$\begin{aligned}\langle\psi_i\psi_j|1/r_{12}|\psi_a\psi_b\rangle=&\int\int\psi_i^*(1)\psi_j^*(2)(1/r_{12})\\&\times\left[\psi_a(1)\psi_b(2)-\psi_b(1)\psi_a(2)\right]\,d1d2\,.\end{aligned} \tag{2.14}$$

This makes it obvious that the present OEP energy expression reduces to the HF energy expression in the absence of correlation, so the generalized OEP problem treated here reduces to the classic OEP problem of Sharp and Horton [1] and Talman and Shadwick [2] when correlation is neglected.

C. OEP equation

Having carefully defined the optimized effective exchange-correlation potential, it remains to develop a useful equation for finding this OEP.

This requires the solution of Eq. (2.10) which may be expanded as

$$0 = \frac{\delta E_{\rm OEP}[G_{\rm OEP}]}{\delta v_{\rm xc}^{\rm OEP}(\mathbf{r})} = \int\int\int \frac{\delta E_{\rm OEP}}{\delta G_{\rm OEP}(1,2;\omega)} \frac{\delta G_{\rm OEP}(1,2;\omega)}{\delta v_{\rm xc}^{\rm OEP}(\mathbf{r})}\, d1d2d\omega. \tag{2.15}$$

The first derivative under the integral signs can be evaluated with the help of Eqs. (2.2) and (2.4),

$$\frac{\delta E_{\rm OEP}[G_{\rm OEP}]}{\delta G_{\rm OEP}(1,2;\omega)} = \frac{e^{i\eta\omega}}{2\pi i}\{M(2,1;\omega;G_{\rm OEP}] + \omega\delta(2-1)\}\,. \tag{2.16}$$

The derivative $\delta G_{\rm OEP}/\delta v_{\rm xc}^{\rm OEP}(\mathbf{r})$ can be derived beginning from the identity

$$\int G_{\rm OEP}(1,2;\omega)G_{\rm OEP}^{-1}(2,3;\omega)\, d2 = \delta(1-3)\,, \tag{2.17}$$

which implies that

$$\frac{\delta G_{\rm OEP}(1,2;\omega)}{\delta v_{\rm xc}^{\rm OEP}(\mathbf{r})} = -\int\int G_{\rm OEP}(1,3;\omega)\frac{\delta G_{\rm OEP}^{-1}(3,4;\omega)}{\delta v_{\rm xc}^{\rm OEP}(\mathbf{r})} \times G_{\rm OEP}(4,2;\omega)\, d3d4. \tag{2.18}$$

Now, from Eqs. (2.6) and (2.7),

$$\frac{\delta\,(G_{\rm OEP})^{-1}(1,2;\omega)}{\delta v_{\rm xc}^{\rm OEP}(\mathbf{r})} = -\delta(\mathbf{r}-\mathbf{r}_1)\delta(1-2)\,, \tag{2.19}$$

so

$$\frac{\delta G_{\rm OEP}(1,2;\omega)}{\delta v_{\rm xc}^{\rm OEP}(\mathbf{r})} = \sum_\sigma G_{\rm OEP}(1,\mathbf{r}\sigma;\omega)G_{\rm OEP}(\mathbf{r}\sigma,2;\omega). \tag{2.20}$$

Inserting Eqs. (2.16) and (2.20) into Eq. (2.15) gives

$$0 = \sum_\sigma \frac{1}{2\pi i}\oint_U \int\int G_{\rm OEP}(\mathbf{r}\sigma,2;\omega)\,\{\Sigma^{\rm xc}(2,1;\omega;G_{\rm OEP}] - v_{\rm xc}^{\rm OEP}(\mathbf{r}_1)\delta(2-1) + \omega\delta(2-1)\} \times G_{\rm OEP}(1,\mathbf{r}\sigma;\omega)\, d1d2d\omega\,, \tag{2.21}$$

where the relation

$$M(2,1;G_{\rm OEP}] = \Sigma^{\rm xc}(2,1;\omega;G_{\rm OEP}] - v_{\rm xc}^{\rm OEP}(\mathbf{r}_1)\delta(2-1) \tag{2.22}$$

has been used. (The factor of $e^{i\eta\omega}$ has been absorbed in forming the contour integral.) Since the $\omega\delta(2-1)$ term disappears when the contour integration is performed, the final OEP equation is

$$0 = \sum_\sigma \frac{1}{2\pi i}\oint_U \int\int G_{\rm OEP}(\mathbf{r}\sigma,2;\omega)\{\Sigma^{\rm xc}(2,1;\omega;G_{\rm OEP}] - v_{\rm xc}^{\rm OEP}(\mathbf{r}_1)\delta(2-1)\}G_{\rm OEP}(1,\mathbf{r}\sigma;\omega)\, d1d2d\omega\,. \tag{2.23}$$

Comparison with Eq. (1.5) shows that this is just the linear response Sham-Schlüter equation and thus $v_{\rm xc}^{\rm OEP}$ may be identified with the exact Kohn-Sham exchange-correlation potential $v_{\rm xc}^{\rm KS}$ (within the linear response approximation to the Sham-Schlüter equation). This identification means that $v_{\rm xc}^{\rm KS}$ can now be interpreted as the variationally best local approximation to the exchange-correlation self-energy $\hat{\Sigma}^{\rm xc}(\omega)$. Note that this confirms previous conjectures that density-functional approximations for the self-energy intended to improve upon the (exact) Kohn-Sham potential will have to be nonlocal in time [25–27] and/or in space [28–30].

It is worth emphasizing that the fact that the (linear response) difference between the Kohn-Sham and the true charge densities is zero has *not* been used in the present derivation. Rather, here, it emerges as a consequence of the imposition of the locality constraint in a variational many-body theory energy expression. This is in contrast to the work of Sham *et al.* which is based on the requirement that the Kohn-Sham and true charge densities are equal. It is the fact that these two different approaches yield the same equation for $v_{\rm xc}$ (in the linear response approximation) that allows $v_{\rm xc}$ to be interpreted as the variationally best local approximation to the nonlocal (in space and time) exchange-correlation self-energy operator $\hat{\Sigma}^{\rm xc}(\omega)$.

It also seems worth mentioning the connection with the widely used Møller-Plesset form of many-body perturbation theory. As was mentioned in Sec. II A, the Møller-Plesset energy expression is the same as Klein's energy expression up to second order. Thus it might seem that the derivation could have been carried out directly starting from the Møller-Plesset expression without recourse to Green functions. Indeed, the result obtained here can also be obtained, to second order, by taking the variation of the Møller-Plesset energy expression with respect to the orbitals of a local potential. However, in order to see why the orbital energies do not enter into this variation, a return to the Green function formalism, and Eq. (2.15) in particular, is required. It is then seen that the infinitesimals, $i\eta$, used in evaluating the contour integrals cause terms arising from variations over the orbital energies to cancel out.

III. QUASIPARTICLE LIMIT AND FURTHER APPROXIMATIONS

One objective of OEP work, which has already been touched upon in the present paper, is the use of the OEP to obtain an improved conceptual understanding of the exact exchange-correlation potential. In this sec-tion, the Sharp-Horton–Krieger-Li-Iafrate approximation to $v_{\rm xc}$ (itself a correction to Slater's original concept) is generalized to include correlation in the quasiparticle limit. This involves the use of certain approximations which are invoked for the insight they provide, rather than their quantitative accuracy.

The first step in this direction is to carry out the contour integrations and rewrite the OEP equation (2.23) as an exact matrix equation in the orthonormal basis of OEP orbitals. This gives

$$\begin{aligned}\sum_\sigma \sum_{ia} \psi_i^{\rm OEP}(\mathbf{r}\sigma)\psi_a^{\rm OEP*}(\mathbf{r}\sigma)\frac{(v_{\rm xc}^{\rm OEP})_{ia}}{\epsilon_i^{\rm OEP}-\epsilon_a^{\rm OEP}} + \text{c.c.} &= \sum_\sigma \sum_{ia} \psi_i^{\rm OEP}(\mathbf{r}\sigma)\psi_a^{\rm OEP*}(\mathbf{r}\sigma)\frac{\Sigma_{ia}^x + \Sigma_{ia}^h(\epsilon_a^{\rm OEP}) + \Sigma_{ia}^p(\epsilon_i^{\rm OEP})}{\epsilon_i^{\rm OEP}-\epsilon_a^{\rm OEP}} + \text{c.c.} \\ &\quad + \sum_\sigma \sum_{i<j} \psi_i^{\rm OEP}(\mathbf{r}\sigma)\psi_j^{\rm OEP*}(\mathbf{r}\sigma)\frac{\Sigma_{ij}^p(\epsilon_i^{\rm OEP}) - \Sigma_{ij}^p(\epsilon_j^{\rm OEP})}{\epsilon_i^{\rm OEP}-\epsilon_j^{\rm OEP}} + \text{c.c.} \\ &\quad + \sum_\sigma \sum_{a<b} \psi_a^{\rm OEP}(\mathbf{r}\sigma)\psi_b^{\rm OEP*}(\mathbf{r}\sigma)\frac{\Sigma_{ab}^h(\epsilon_b^{\rm OEP}) - \Sigma_{ab}^h(\epsilon_a^{\rm OEP})}{\epsilon_a^{\rm OEP}-\epsilon_b^{\rm OEP}} + \text{c.c.}\,,\end{aligned} \tag{3.1}$$

where c.c. denotes the complex conjugate of the previous term, the exchange-correlation self-energy

$$\mathbf{\Sigma}^{\rm xc}(\omega) = \mathbf{\Sigma}^x + \mathbf{\Sigma}^c(\omega) \tag{3.2}$$

has been divided into its energy-independent exchange part and its energy-dependent correlation part, and the correlation part has been divided into two parts which correspond roughly to "hole" and "particle" parts,

$$\mathbf{\Sigma}^c(\omega) = \mathbf{\Sigma}^h(\omega) + \mathbf{\Sigma}^p(\omega)\,. \tag{3.3}$$

Specifically, provided that $\mathbf{\Sigma}^c(\omega)$ has only simple poles,

$$\mathbf{\Sigma}^h(1,2;\omega) = \sum_I \frac{R_I(1,2)}{\omega - \omega_I - i\eta} \tag{3.4}$$

and

$$\mathbf{\Sigma}^p(1,2;\omega) = \mathbf{\Sigma}^c(1,2;\omega) - \mathbf{\Sigma}^h(1,2;\omega)\,, \tag{3.5}$$

where ω_I and R_I denote the poles and corresponding residues in the upper half complex ω plane.

In the absence of correlation, Eq. (3.1) for the exchange-correlation potential $v_{\rm xc}^{\rm OEP}$ reduces to the corresponding equation for the exchange potential familiar from HF OEP work. However, the effect of including correlation is not simply to replace Σ^x with $\Sigma^{\rm xc}(\omega)$ in the HF OEP equation, but rather yields an exchange-correlation OEP equation with a more complicated structure. This is hardly surprising. Nevertheless, in the limit of a self-energy which is a slowly varying function of ω (quasiparticle limit), Eq. (3.1) for $v_{\rm xc}^{\rm OEP}$ does reduce to a simpler equation analogous to that for the exchange-only case. In this regime, terms involving derivatives of $\Sigma^{\rm xc}(\omega)$,

$$\left(\frac{\partial \Sigma_{rs}^{\rm xc}}{\partial \omega}\right)_{\omega=(\epsilon_r^{\rm OEP}+\epsilon_s^{\rm OEP})/2} \approx \frac{\Sigma_{rs}^{\rm xc}(\epsilon_r^{\rm OEP}) - \Sigma_{rs}^{\rm xc}(\epsilon_s^{\rm OEP})}{\epsilon_r^{\rm OEP}-\epsilon_s^{\rm OEP}}\,, \tag{3.6}$$

are negligible. For present purposes, it is assumed that this approximation is valid over the entire energy range. Realistically, however, the quasiparticle regime rarely spans the entire range of occupied orbital energies. Thus, here, it is probably best to think of this approximation being applied to somewhat more artificial systems such as molecular calculations which are restricted to an active space of outer valence orbitals (presumably through the use of effective core potentials) or calculations using certain simplified self-energy approximations such as the Coulomb hole and screened exchange (COHSEX) approximation [23,29]. Assuming that the hole and particle parts of the self-energy are individually slowly varying, and adding and subtracting $\Sigma_{ia}^h(\epsilon_i^{\rm OEP})$ (or its complex conjugate) to the numerators of the coefficients in the first line of the right hand side of Eq. (3.1), gives

$$\begin{aligned}\sum_\sigma \sum_{ia} \psi_i^{\rm OEP}(\mathbf{r}\sigma)\psi_a^{\rm OEP*}(\mathbf{r}\sigma)\frac{(v_{\rm xc}^{\rm OEP})_{ia}}{\epsilon_i^{\rm OEP}-\epsilon_a^{\rm OEP}} + \text{c.c.} \\ = \sum_\sigma \sum_{ia} \psi_i^{\rm OEP}(\mathbf{r}\sigma)\psi_a^{\rm OEP*}(\mathbf{r}\sigma)\frac{\Sigma_{ia}^{\rm xc}(\epsilon_i^{\rm OEP})}{\epsilon_i^{\rm OEP}-\epsilon_a^{\rm OEP}} + \text{c.c.}\end{aligned} \tag{3.7}$$

This is the simple analog of the HF OEP equation, with the exchange self-energy replaced by the exchange-correlation self-energy. Note that the correlation effects that remain in the quasiparticle limit come from the particle-hole cross terms, while the particle-particle and hole-hole contributions are negligible in this approximation.

There is a certain arbitrariness in going from Eq. (3.1) to Eq. (3.7), in that one could just as well have added and subtracted $\Sigma_{ia}^p(\epsilon_a^{\rm OEP})$, instead of $\Sigma_{ia}^h(\epsilon_i^{\rm OEP})$, in which case $\Sigma_{ia}^{\rm xc}$ in Eq. (3.7) would be evaluated at $\epsilon_a^{\rm OEP}$ instead of at $\epsilon_i^{\rm OEP}$. Of course the difference between these two equations is again a derivative of $\Sigma^{\rm xc}$, which is negligible in the quasiparticle approximation. However, the choice of $\epsilon_i^{\rm OEP}$ is appealing from the point of view of finding an (approximate) form for the exchange-correlation potential which depends, like the density, only on occupied orbitals. Such an approximation will be given in Eq. (3.14).

First, however, note that the dependence on *occupied* orbital energies arises naturally in an alternative derivation of Eq. (3.7) within the quasiparticle approximation, where Dyson's equation becomes

$$\{\hat{h}_H[n_{\rm OEP}] + v_{\rm xc}^{\rm OEP} + [\hat{\Sigma}^{\rm xc}(\epsilon_r^{\rm OEP}) - v_{\rm xc}^{\rm OEP}]\}\psi_r = \omega_r\psi_r\,. \tag{3.8}$$

As was shown in Sec. II C, the OEP equation (2.23) (equivalently the linear response Sham-Schlüter equation) is equivalent to the statement that the linear response of the charge density to the perturbation $[\hat{\Sigma}^{\rm xc}(\omega) - v_{\rm xc}^{\rm OEP}]$ is zero. Here it is convenient to use the density condition

$$0 = \delta n_{\rm OEP}(\mathbf{r}) = \sum_\sigma \sum_i [\psi_i^{\rm OEP}(\mathbf{r}\sigma)\delta\psi_i^*(\mathbf{r}\sigma) + \text{c.c.}]\,. \tag{3.9}$$

The sum over i is, of course, only over occupied orbitals and

$$\delta\psi_i(1) = \sum_r^{r\neq i} \psi_r^{\rm OEP}(1)\frac{\langle\psi_r^{\rm OEP}|\hat{\Sigma}^{\rm xc}(\epsilon_i^{\rm OEP}) - v_{\rm xc}^{\rm OEP}|\psi_i^{\rm OEP}\rangle}{\epsilon_i^{\rm OEP} - \epsilon_r^{\rm OEP}}\,. \tag{3.10}$$

After rearrangement, Eq. (3.9) becomes

$$\begin{aligned}\sum_\sigma\sum_{ia}\psi_i^{\rm OEP}(\mathbf{r}\sigma)\psi_a^{\rm OEP*}(\mathbf{r}\sigma)\frac{(v_{\rm xc}^{\rm OEP})_{ia}}{\epsilon_i^{\rm OEP} - \epsilon_a^{\rm OEP}} + \text{c.c.} &= \sum_\sigma\sum_{ia}\psi_i^{\rm OEP}(\mathbf{r}\sigma)\psi_a^{\rm OEP*}(\mathbf{r}\sigma)\frac{\Sigma_{ia}^{\rm xc}(\epsilon_i^{\rm OEP})}{\epsilon_i^{\rm OEP} - \epsilon_a^{\rm OEP}} + \text{c.c.}\\ &\quad + \sum_\sigma\sum_{i<j}\psi_i^{\rm OEP}(\mathbf{r}\sigma)\psi_j^{\rm OEP*}(\mathbf{r}\sigma)\frac{\Sigma_{ij}^{\rm xc}(\epsilon_i^{\rm OEP}) - \Sigma_{ij}^{\rm xc}(\epsilon_j^{\rm OEP})}{\epsilon_i^{\rm OEP} - \epsilon_j^{\rm OEP}} + \text{c.c.}\end{aligned} \tag{3.11}$$

Since this is in the quasiparticle regime, the last line, which involves only derivatives of the exchange-correlation self-energy, can be neglected and Eq. (3.7) results. Of course, in the exchange-only case this involves no approximation at all, since $\hat{\Sigma}^x$ is energy independent.

In a footnote, Sharp and Horton(SH) [1] proposed an approximation to their OEP equation that was subsequently elaborated by Krieger, Li, and Iafrate (KLI) [21,22]. This SH-KLI approximation was found to work surprisingly well in the exchange-only case and can now easily be applied to the exchange-correlation case in the quasiparticle approximation. It simply consists of approximating the denominators in Eq. (3.7) by an average orbital energy difference, which then cancels out, leaving

$$\sum_\sigma\sum_{ia}\psi_i^{\rm OEP}(\mathbf{r}\sigma)\psi_a^{\rm OEP*}(\mathbf{r}\sigma)(v_{\rm xc}^{\rm OEP})_{ia} + \text{c.c.} = \sum_\sigma\sum_{ia}\psi_i^{\rm OEP}(\mathbf{r}\sigma)\psi_a^{\rm OEP*}(\mathbf{r}\sigma)\Sigma_{ia}^{\rm xc}(\epsilon_i^{\rm OEP}) + \text{c.c.} \tag{3.12}$$

Using the orbital completeness relation,

$$\begin{aligned}\sum_a \psi_a^{\rm OEP}(1)M_{ai} &= \sum_a \psi_a^{\rm OEP}(1)\langle\psi_a^{\rm OEP}|\hat{M}|\psi_a^{\rm OEP}\rangle\\ &= \left(\hat{1} - \sum_j \psi_j^{\rm OEP}(1)\langle\psi_j^{\rm OEP}|\right)\hat{M}|\psi_i^{\rm OEP}\\ &= \hat{M}\psi_i^{\rm OEP}(1) - \sum_j \psi_j^{\rm OEP}(1)M_{ji}\,,\end{aligned} \tag{3.13}$$

where $\hat{M}$ is $v_{\rm xc}^{\rm OEP}$ or $\hat{\Sigma}^{\rm xc}$, then allows Eq. (3.12) to be rewritten as

$$v_{\rm xc}^{\rm OEP}(\mathbf{r}) = \frac{\sum_\sigma\sum_i {\rm Re}\{\psi_i^{\rm OEP*}(\mathbf{r}\sigma)\hat{\Sigma}^{\rm xc}(\epsilon_i^{\rm OEP})\psi_i^{\rm OEP}(\mathbf{r}\sigma)\}}{\sum_\sigma\sum_i|\psi_i^{\rm OEP}(\mathbf{r}\sigma)|^2} - \frac{\sum_\sigma\sum_i\langle\psi_i^{\rm OEP}|\hat{\Sigma}^{\rm xc}(\epsilon_i^{\rm OEP}) - v_{\rm xc}^{\rm OEP}|\psi_i^{\rm OEP}\rangle|\psi_i^{\rm OEP}(\mathbf{r}\sigma)|^2}{\sum_\sigma\sum_i|\psi_i^{\rm OEP}(\mathbf{r}\sigma)|^2}\,. \tag{3.14}$$

The first term on the right hand side is simply the exchange-correlation version of Slater's original local exchange potential [14] while the second term includes the first-order orbital energy correction,

$$\omega_i = \epsilon_i^{\rm OEP} + \langle\psi_i^{\rm OEP}|\hat{\Sigma}^{\rm xc}(\epsilon_i^{\rm OEP}) - v_{\rm xc}^{\rm OEP}|\psi_i^{\rm OEP}\rangle\,, \tag{3.15}$$

whose importance has been well illustrated in Refs. [21,22] for the exchange-only case.

IV. CONCLUDING DISCUSSION

In the present paper, the HF OEP model of Sharp and Horton and of Talman and Shadwick has been generalized to treat the correlated case, through the use of a variational energy expression which is a functional of the Green function. This variational approach is complementary to the approach of Sham and Schlüter [3] and Sham [13] who used the fact that the Kohn-Sham orbitals must yield the true charge density to give an equation for the exact Kohn-Sham exchange-correlation potential. The fact that these two different approaches yield the same equation for the potential (in the linear response approximation) then allows the Kohn-Sham v_{xc} to be interpreted as the variationally best local approximation to $\hat{\Sigma}^{\mathrm{xc}}(\omega)$.

One consequence of this is that attempts to improve on v_{xc} as an approximation to $\hat{\Sigma}^{\mathrm{xc}}(\omega)$ should involve nonlocality either in space or in time. Since energy dependence of the potential is more difficult to handle computationally than is spatial nonlocality, it is interesting to consider the possibility of lifting the constraint of locality in space, while still requiring locality in time, to obtain an optimized effective nonlocal potential (OENP). The resulting OENP equation

$$\begin{aligned} 0 = \frac{1}{2\pi i} \oint_{U} \int \int & G_{\mathrm{OENP}}(1,3;\omega) \\ & \times \{\Sigma^{\mathrm{xc}}(3,4;\omega;G_{\mathrm{OEP}}] - v_{\mathrm{xc}}^{\mathrm{OENP}}(3,4)\} \\ & \times G_{\mathrm{OENP}}(4,2;\omega)\, d3d4d\omega \end{aligned} \tag{4.1}$$

or equivalently

$$\delta\gamma(1,2) = 0 \tag{4.2}$$

states that the linear response of the one-particle density matrix to the perturbation $[\hat{\Sigma}^{\mathrm{xc}}(\omega;G^{\mathrm{OENP}}) - v_{\mathrm{xc}}^{\mathrm{OENP}}]$ is zero, as compared to a corresponding statement about the density in the OEP equation (2.23). One might expect that there would be no solution of this equation for $v_{\mathrm{xc}}^{\mathrm{OENP}}$, except if correlation were neglected [in which case $\hat{\Sigma}^{\mathrm{xc}}(\omega) = \hat{\Sigma}^{\mathrm{x}} = v_{\mathrm{xc}}^{\mathrm{OENP}}$], because the eigenvalues (natural orbital occupation numbers) of correlated and independent-particle density matrices are very different. Nevertheless, a first-order variation does vanish in some cases. The OENP analog of Eq. (3.1) involves direct product functions rather than simple products, with the result that no solution $v_{\mathrm{xc}}^{\mathrm{OENP}}$ exists unless the particle-particle and hole-hole terms vanish. This is the case for the homogeneous electron gas, and is also true in the quasiparticle limit, where the self-energy is a slowly varying function of energy. However, unlike the spatially local case, no solution for the OENP exists in the general correlated case.

Returning now to the fully local case, the present derivation of the OEP, taken together with the Sham-Schlüter equation for the exact Kohn-Sham v_{xc}, can be regarded as an alternative derivation of the Kohn-Sham equation, as the variationally best local approximation to the Dyson quasiparticle equation. This derivation is approximate, insofar as it involves the linear response approximation to the Sham-Schlüter equation. Nevertheless, it is interesting from the point of view of interpretation. In the Kohn-Sham derivation, the orbitals are introduced as a physically fictitious, mathematical device. Here, on the other hand, it is natural to consider the Kohn-Sham orbitals and orbital energies as approximations to the Dyson orbitals and orbital energies. Whether this approximation is good enough to be useful is another question, and one which can really only be answered computationally. The infamous band-gap problem is not very encouraging with regard to the quality of the Kohn-Sham orbital energies themselves, as approximate Dyson orbital energies. Because of the problem of derivative discontinuities pointed out by Perdew and Levy [31], it is to be expected that some correction beyond a local potential is needed in order to obtain a good approximation to the Dyson orbital energies. Indeed, first-order corrections to the Kohn-Sham orbital energies have been found to yield a considerable improvement [32]. However, this difficulty with the orbital energies does not imply that the Kohn-Sham orbitals are necessarily poor approximations to the Dyson orbitals. Indeed, even if every Dyson orbital were identical to some Kohn-Sham orbital, the corresponding orbital energies could still differ by an orbital-dependent constant, as is easily seen by subtracting the Kohn-Sham equation from the Dyson equation. [In this context, it is interesting to note that the energy expression (2.12) depends more heavily on the orbitals than on the orbital energies.] In the correlated case, both the number and normalization of Kohn-Sham orbitals differ from that for Dyson orbitals, so the approximation of Dyson orbitals by Kohn-Sham orbitals means a many-to-one correspondence in which each Dyson orbital is proportional to some Kohn-Sham orbital, with the proportionality constant given by the spectroscopic factor. This is analogous to the "target Hartree-Fock approximation," commonly used in analyzing spectra [33], where Hartree-Fock orbitals are used as approximate Dyson orbitals. This "target Kohn-Sham approximation" is presented in detail in Ref. [34], where the practical utility of Kohn-Sham orbitals as approximate Dyson orbitals, for calculating electron momentum spectroscopy triple differential cross sections, is investigated.

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