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Physical interpretation and assessment of the Coulomb-hole and screened-exchange approximation for molecules

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Hedin's Coulomb-hole and screened-exchange (COHSEX) approximation for the one-electron Green-function self-energy is examined for small molecules through second order in the bare interaction (COHSEX2). Numerical examples suggest that the COHSEX2 approximation works better for ionization potentials and generalized overlaps (Dyson amplitudes) than does either Koopman's theorem or the usual second-order Green-function (GF2) approximation. This result has been traced to the superior quality of Hedin's GW approximation evaluated to second order in the bare interaction ($GW2$). (The GW self-energy is the simple product of the Green function G and the screened interaction W in the time-and-position space representation.) The COHSEX2 approximation is found to be a rather crude approximation for the $GW2$ self-energy at the center of the highest occupied molecular orbital–lowest unoccupied molecular orbital energy gap, but is still superior to the GF2 approximation in most of our calculated results and is amenable to limited dynamical corrections. The primary potential advantage of the COHSEX approximation over the GW approximation is that no sums over virtual orbitals need be performed once the static screened interaction or polarization is known. Our results suggest that accurate density-functional approximations for the static screened interaction or polarization can lead to self-energies of accuracies beyond both Koopmans's theorem and the GF2 level.

I. INTRODUCTION

The Green-function (GF) method is a well-known way to reduce an n-electron problem to a pseudo-one-electron problem, namely Dyson's quasiparticle equation. The important many-body effects are contained in a pseudopotential known as the self-energy. Once this potential is calculated, the one-electron quasiparticle equation may then be solved to give ionization spectra,[1] scattering cross sections,[2] and ground-state properties.[3,4] Although elaborate and accurate approximations for the self-energy are known,[1,2,5-7] it is clear that less elaborate, less computationally intensive approximations are also useful. A relatively simple self-energy approximation which has been found to be useful for the electronic structure of solids, but which has not been applied to atomic and molecular problems, is Hedin's Coulomb-hole and screened-exchange (COHSEX) approximation. This paper contains our assessment of the COHSEX approximation as evaluated to second order in the bare interaction and applied to the calculation of ionization potentials and generalized overlaps of small molecules.

The COHSEX approximation is a linear response ap-

proximation for the self-energy. Its principal advantage is that the self-energy can be calculated directly from a knowledge of the static polarization without the complication of summations or integrations over virtual orbitals. The original purpose of the COHSEX approximation[8,9] was to provide a physically interpretable approximation to a more sophisticated approximation (the GW approximation in which the self-energy is a product of the Green function G and the screened interaction W), and this physical insight should not be overlooked. Nevertheless, it was immediately recognized that the COHSEX approximation had the aforementioned computational advantage. This is particularly true when the diagonal (in momentum space) approximation is used, since the only additional information needed is the (static) dielectric constant for the solid. Thus, it is not surprising that the COHSEX approximation was soon implemented by several workers,[10-18] and is now reasonably well characterized for solids. Thus, it is known that the COHSEX approximation works best near the Fermi surface and appears capable of producing quite good direct band gaps, although absolute energies and indirect band gaps are of lower quality. This is fortunate because

the primary motivation in recent years for studying the COHSEX approximation has been the failure of the Kohn-Sham (ground-state) density-functional theory to obtain satisfactory band gaps[19]—a problem for which the COHSEX approximation appears to be ideally suited.[18]

Calculation of the static polarization is the obvious primary obstacle in the way of useful molecular applications of the COHSEX approximation. If the static polarization is calculated via the many-body perturbation theory, then the COHSEX approximation has the advantage of eliminating one of the sums over virtual orbitals. However, it should be kept in mind that several such sums may have already been used in the perturbation theory evaluation of the static polarization. An alternative procedure is to evaluate the static polarization via density-functional techniques. A naive approach likely to be valid for slowly varying densities, is to simply borrow the well-known static polarization for the homogeneous electron gas (Ref. 20, pp. 151–167) with the same density as the local density. This approach is entirely consistent with recent work on semiconductors which emphasizes the similarity between the electron-gas self-energy and semiconductor self-energies in the center of the band gap,[21] but seems less likely to be useful for molecules. A better approach is to use Kohn-Sham density-functional theory[22] to calculate the static linear response. This has been performed by Zangwill and Soven for atoms[23] and by Levine and Soven for molecules[24] with gratifying results both in terms of quantitativeness and efficiency of the calculations. The COHSEX approximation would allow these results to be extended directly to provide a density-functional approximation for the self-energy. However, the limits of such an approximation are the limits of the COHSEX approximation itself. The purpose of the present paper is to define the limits of the COHSEX approximation for molecules. In particular, the density-functional theory is not used in any of the formalisms or computations presented in this paper.

For completeness, we also list other prominent methods which could be construed to be density functionals for the self-energy. The Kohn-Sham exchange-correlation potential has been confused with the self-energy[25] essentially from the inception of Kohn-Sham theory.[22] This confusion continues despite equally early work of Sham and Kohn[26] who pointed out that the two concepts were not identical and who proposed an altogether different local density functional for the self-energy, valid only for the case of slowly varying density. A modified version of the Sham-Kohn strategy has been applied to solids with encouraging results.[27,28] Slater's transition orbital approximation[29] applied within the density-functional theory method provides a modified exchange-correlation potential which serves a similar role as the self-energy, but the approximation is known to fail for extended systems.[29] Finally, self-interaction corrected[19,30] Kohn-Sham theory provides what may be construed to be an orbital-dependent local self-energy. All of these have proven useful in the calculation of ionization potentials and/or band spectra, but are less well characterized as self-energies for other applications (e.g., scattering cross sections). In contrast to these approxi-

mations, the COHSEX approximation is a nonlocal approximation. It has the important role as a rigorous Green-function approximation lying intermediate between more elaborate Green-function approximations and less understood density-functional approximations. As such, it provides a relatively simple useful tool when the conventional density-functional theory fails.[18]

The remainder of the paper is divided as follows. The Green-function method and COHSEX approximation are reviewed in Sec. II. Special emphasis is placed on a clear picture of the physics and mathematical structure of the self-energy (although much of this is review) because of the central importance of such a picture in defining the limitations of the approximation. Modifications for molecular applications are discussed in detail. Section III contains the results of our numerical study. The main emphasis is on ionization potentials since these are readily compared with better calculations and experimental data. However, we also report some generalized overlap calculations using the COHSEX and related methods. Our conclusions are summarized in Sec. IV.

II. FORMALISM

We review the physics and formalism associated with the self-energy. Ideas are gathered from the solid state, atomic and molecular scattering, and the bound-state theory with the aim of clarifying the underlying physics. Note that our ultimate emphasis is the ionization spectra of small molecules and that we will tend to ignore complications arising from nonsquare integrable continuum functions (needed in scattering theory).

A. Dyson's quasiparticle equation

Dyson's quasiparticle equation[31] (QPE) for a molecule M simultaneously describes vertical ionization

$$M \rightarrow M^+ + e^- \ ,$$
$$\Psi^{(n)} \rightarrow \Psi_i^{(n-1)} \ , \tag{2.1}$$

and vertical electron attachment

$$M + e^- \rightarrow M^- \ ,$$
$$\Psi^{(n)} \rightarrow \Psi_i^{(n+1)} \ , \tag{2.2}$$

via the many-body theory using the second-quantized form of the electronic Hamiltonian (which is, of course, independent of electron number). When Møller-Plesset partitioning[32] is employed, the QPE is

$$[\hat{F} + \hat{\Sigma}(\omega)]\phi = \omega\phi \ , \tag{2.3}$$

where $\hat{F}$ is the Fock operator for the neutral molecule M and $\hat{\Sigma}(\omega)$ is the self-energy. Møller-Plesset partitioning is the prevalent choice in the molecular physics literature (although Epstein-Nesbet partitioning[33] is also used) and is the only choice considered in this paper. The QPE is a generalized eigenvalue problem whose solutions fall into two classes. If the ith ionization potential and ith electron affinity are denoted by I_i and A_i, respectively, then the "ionization solutions" satisfy

$$\omega = -I_i \ ,$$

$$\sqrt{S} \ \phi(1) = \langle \Psi_i^{(n-1)} | \hat{\psi}(1) | \Psi^{(n)} \rangle \qquad (2.4)$$

while the "electron affinity solutions" satisfy

$$\omega = -A_i \ ,$$

$$\sqrt{S} \ \phi(1) = \langle \Psi^{(n)} | \hat{\psi}(1) | \Psi_i^{(n+1)} \rangle \ , \qquad (2.5)$$

where in both cases,

$$S = \left[1 - \left\langle \phi \left| \frac{d\hat{\Sigma}(\omega)}{d\omega} \right| \phi \right\rangle \right]^{-1} , \quad \langle \phi | \phi \rangle = 1 \qquad (2.6)$$

defines the spectroscopic factor S [and $\hat{\psi}(1)$ is the field annihilation operator]. Note that here and throughout, numerical variables (e.g., $1,1',2,\ldots$) refer to space and spin coordinates *but not time*. The spectroscopic factors play a prominent role in the interpretation of photoelectron spectra[1] while the generalized overlaps ϕ are important for electron momentum spectroscopy (Ref. 34 and references contained therein).

The self-energy includes all the important many-body effects. When it is set equal to zero in the QPE, the simple Koopmans's theorem[35] picture is recovered in Eqs. (2.4)–(2.6).

The physical nature of these many-body effects may be understood by reference to the scattering theory.[36] Most of the electron affinity solutions are, in fact, continuum states. Thus, the QPE Hamiltonian describes the dynamics of a scattering electron. Since scattering can involve polarization of the scatterer and induced excitations (i.e., multichannel effects), these must also be described by the self-energy. Only the polarization physics is retained in the COHSEX approximation. The multichannel effects are manifested in the rather complicated dynamical behavior of the self-energy at higher energies, as will be further elaborated upon in Sec. II C.

For completeness, we mention that a complication in the physics of the self-energy comes from the requirement that the energy have an imaginary component which gives the lifetime of the continuum state. This requires the self-energy to be non-Hermitian [and complicates the simple interpretation given in Eqs. (2.4) and (2.5)]. However, when a finite L^2 basis is used, the self-energy should be Hermitian since only infinite lifetime (i.e., bound) states are described. Since we are concerned exclusively with parent and ion bound states, we can confine ourselves to the L^2 case. (Note, however, that some scattering applications are still viable within the L^2 approximation provided proper precautions are taken.[37,38])

B. COHSEX approximation

Successful methods for generating self-energy approximations include the superoperator or equations-of-motion method,[5,6] the diagrammatic method,[1,7] and the functional derivative method.[2,8,9] These three methods are all complementary, but the functional derivative method has a special physical appeal resulting from considerations of arbitrary small external perturbations. This was Hedin's starting point for the "Coulomb-hole

and screened-exchange" approximation which we will now describe.

Following Martin and Schwinger,[39] Hedin examined the response to the introduction of a finite local one-electron perturbation which is later set equal to zero. This leads to four coupled equations involving the exact Green function, the self-energy, the screened interaction, the polarization propagator, and the vertex function. Elimination of the polarization propagator and the vertex function then leads to an infinite exact (if convergent) series for the self-energy in terms of the Green function and the screened interaction. This is significant because the screened interaction W plus the bare potential

$$W_p(1,2;\omega) = W(1,2;\omega) - \frac{1}{r_{12}} = \int \frac{\Delta\rho(3,2;\omega)}{r_{13}} d3 \qquad (2.7)$$

has a ready physical interpretation in terms of linear response theory [provided the signs of certain infinitesimals can be ignored (Ref. 20, p. 77)]. (Atomic units are used throughout, unless otherwise specified.) Specifically, in the static case when $\omega = 0$, W_p is the potential acting on r_1 due to the linear response of the charge density $\Delta\rho(3,2;0)$ created by the introduction of a unit charge at r_2. In the dynamic case, W_p is interpretable in terms of the Fourier components of the linear response of the charge density due to the introduction of a unit charge impulse $\delta(t-t_0)/r_{13}$ at r_2.

For solids and the electron gas, it is usual to ignore all but the linear term in the screened interaction in the exact expansion of the self-energy. This is the GW approximation[8,9] and is particularly appealing in the position representation where only a simple convolution *of the frequency variable* is necessary

$$\Sigma(1,2;\omega) = \frac{i}{2\pi} \int e^{+i\eta\omega_0} G(1,2;\omega+\omega_0) W_p(1,2;\omega_0) d\omega_0 \ , \qquad (2.8)$$

where the infinitesimal η may only be set equal to zero *after* the integration. In writing Eq. (2.8), we note that full self-consistency requires that the Fock operator be constructed from the GW density and density matrix — not from the Hartree-Fock quantities. (We will ignore this last point in making the G^0W approximation in Sec. II C.)

The COHSEX approximation consists of the "simple but rough argument" (Ref. 9, p. 40) that the screened interaction is roughly independent of frequency. Hence,

$$\Sigma(1,2;\omega) = \frac{i}{2\pi} W_p(1,2;0) \int \left[\frac{e^{+i\eta\omega_0} + e^{-i\eta\omega_0}}{2} \right]$$

$$\times G(1,2;\omega+\omega_0) d\omega_0$$

$$= \frac{1}{2}\delta(1-2)W_p(1,2;0) - \gamma(1,2)W_p(1,2;0) \ , \qquad (2.9)$$

where $\gamma(1,2)$ is the density matrix normalized to n (the number of electrons in the initial state). We will assess the quality of this approximation in Sec. III. The physical consequences of this approximation become apparent when Eqs. (2.3), (2.7), and (2.9) are combined:

$$[\hat{F}+\hat{\Sigma}(\omega)]\phi(1)=\hat{h}\phi(1)+\int\frac{\rho(2)+[\Delta\rho(2,1;0)/2]}{r_{12}}d2\phi(1)$$

$$-\int\gamma(1,2)\left[\frac{1}{r_{12}}+\int\frac{\Delta\rho(3,2;0)}{r_{13}}d3\right]$$

$$\times\phi(2)d2\ . \qquad (2.10)$$

The result is not very different from the Fock operator acting on ϕ. The first term comprises the kinetic energy plus nuclear attraction. The second term is simply the Coulomb repulsion corrected for the polarization of the charge density ρ by the scattered electron. The third term is the exchange operator with polarization correction. Put another way, the first integral includes the effects of the "Coulomb hole" (COH), while the second integral is the "screened exchange" (SEX).

To summarize, two approximations have been made. First, all but the linear term in the screened interaction in the self-energy expansion has been dropped (i.e., the GW approximation is made). Secondly, the static approximation was made, albeit on somewhat shaky grounds. The result is a formula which incorporates at least some of the polarization physics expected on the basis of our previous discussion.

C. Second-order approximations

Before advancing any further, the screened interaction must be known. We will use an approximate second-order treatment and denote the resulting formulas $GW2$, COHSEX2, etc.

The exact screened interaction may be expressed in terms of the polarization propagator (Ref. 33, p. 110). We will use the lowest-order approximation, which is the polarization propagator for the unperturbed system. Furthermore, we will restrict ourselves to real valued orbitals:

$$W_p(\mathbf{r},\mathbf{r}';\omega)=X_+(\mathbf{r},\mathbf{r}';\omega+i\eta)-X_-(\mathbf{r},\mathbf{r}';\omega-i\eta)\ ,\qquad(2.11)$$

where

$$X_\pm(\mathbf{r},\mathbf{r}';\omega)=\sum_{\substack{i\in O\\b\in V}}\frac{2Y_{ib}(\mathbf{r})Y_{ib}(\mathbf{r}')}{\omega\mp(\varepsilon_b-\varepsilon_i)}\qquad(2.12)$$

and

$$Y_{ib}(\mathbf{r})=\int\frac{\phi_i(\mathbf{r}')\phi_b(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'\ ,\qquad(2.13)$$

where O and V stand for the sets of occupied and virtual orbitals, respectively.

In principle, the self-energy in the GW approximation should be evaluated using the *exact* Green function G (or at least self-consistently). We follow the common practice of approximating G by the zero-order Green function G^0 (i.e., the "G^0W approximation"). This results in

$$\Sigma(\mathbf{r},\mathbf{r}';\omega)=\sum_{\substack{i\in O\\a,b\in V}}\frac{2\phi_a(\mathbf{r})\phi_a(\mathbf{r}')Y_{ib}(\mathbf{r})Y_{ib}(\mathbf{r}')}{[\omega-\varepsilon_a]-\varepsilon_b+\varepsilon_i}$$

$$+\sum_{\substack{i,j\in O\\b\in V}}\frac{2\phi_j(\mathbf{r})\phi_j(\mathbf{r}')Y_{ib}(\mathbf{r})Y_{ib}(\mathbf{r}')}{[\omega-\varepsilon_j]+\varepsilon_b-\varepsilon_i}\qquad(2.14)$$

in the $GW2$ approximation where the infinitessimals have all been set equal to zero.

The COHSEX2 approximation results from setting the square-bracketed terms in the denominators equal to zero in Eq. (2.14). By using the two relations

$$\sum_p\phi_p(\mathbf{r})\phi_p(\mathbf{r}')=\delta(\mathbf{r}-\mathbf{r}')\ ,\qquad(2.15)$$

$$\sum_{j\in O}\phi_j(\mathbf{r})\phi_j(\mathbf{r}')=\gamma(\mathbf{r},\mathbf{r}')\ ,\qquad(2.16)$$

we obtain

$$\Sigma(\mathbf{r},\mathbf{r}';\omega)=\tfrac{1}{2}\delta(\mathbf{r}-\mathbf{r}')W_p(\mathbf{r},\mathbf{r}';0)-\gamma(\mathbf{r},\mathbf{r}')W_p(\mathbf{r},\mathbf{r}';0)$$

$$(2.17)$$

which is precisely the COHSEX approximation [Eq. (2.9)] using the second-order screened interaction. Thus, the static approximation consists of replacing the frequency dependence of the self-energy with the assumption that $\varepsilon_a\approx\omega\approx\varepsilon_i$ for all significant terms in the self-energy expression.

When a finite basis set is used, the completeness relation (2.15) does not hold, and Eq. (2.14) with the brackets set to zero is *not* equivalent to Eq. (2.17). The COHSEX2 calculations reported in Sec. III use Eq. (2.14) with the square-bracket terms set to zero. This is certainly one of the more severe approximations made in this paper, but is not expected to be too severe for our purposes.

The COHSEX approximation clearly ignores several important features of the true self-energy. In particular, multichannel scattering effects are manifested in the poles of the self-energy. A cursory examination of Eq. (2.14) shows that these poles correspond to approximate cation $(i^{-1}j^{-1}b)$ and anion $(i^{-1}ab)$ excitation energies. In the bound-state theory, these poles are essential for calculating correct inner valence ionization potentials (IP's).[34] Since the static approximation removes all poles, it cannot be used for either multichannel scattering or inner valence IP calculations. However, the self-energy is known to be both pole free and slowly varying in the outer valence and low-lying electron affinity region of the molecular binding-energy spectrum. So the static approximation may be useful for low-energy scattering, outer valence ionization, and the first few electron affinities. In fact, the static approximation would appear to be best justified at the center of the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO-LUMO) energy gap

$$\omega=\mu\equiv\tfrac{1}{2}(\varepsilon_{\text{HOMO}}+\varepsilon_{\text{LUMO}})\qquad(2.18)$$

if anywhere, because the energy ω must cancel both the energies of high-lying occupied orbitals and low-lying virtuals.

The COHSEX approximation is also closely linked to the GW approximation. However, the justification for using the GW approximation for molecules is unclear. This becomes most evident when the $GW2$ approximation [Eq. (2.14)] is compared with the usual second-order self-energy formula (which we shall denote as GF2),

$$\Sigma_{sr}(\omega) = \sum_{\substack{i \in O \\ a,b \in V}} \frac{2(as;ib)(ib;ra) - (bs;ai)(ib;ra)}{[\omega - \varepsilon_a] + \varepsilon_i - \varepsilon_b}$$

$$+ \sum_{\substack{i,j \in O \\ b \in V}} \frac{2(sj;ib)(ib;jr) - (is;bj)(ib;jr)}{[\omega - \varepsilon_j] - \varepsilon_i + \varepsilon_b} , \quad (2.19)$$

where

$$(rp;sq) = \int \phi_r(\mathbf{r}_1)\phi_s(\mathbf{r}_2)\frac{1}{r_{12}}\phi_p(\mathbf{r}_1)\phi_q(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 . \quad (2.20)$$

The $GW2$ approximation is obtained from the GF2 approximation by dropping the second term in each numerator in Eq. (2.19) (i.e., neglecting the "exchange diagram"). This neglect could certainly be justified for a high-density electron gas (Ref. 40, pp. 158–164), but it may well be objected that this term is too large to be neglected for small molecules. Indeed, it is standard practice to include the exchange diagram in atomic and molecular physics calculations, even though calculations could be made significantly easier by neglecting it.

However, this objection is somewhat misleading since the point of introducing the screened interaction is to reduce the size of the two-electron interaction. The first two terms in Hedin's exact series are expanded in Feynman diagrams[20,40] in Fig. 1 to consistent order in the screened interaction. The GF2 approximation consists of the $GW2$ approximation (diagrams A and B) plus only a portion (i.e., diagram C) of the term which is second-order in the screened interaction (somewhat arbitrarily denoted the $GWGW$ term). Thus, the GF2 approximation would appear to *overestimate* the $GWGW$ term by evaluating it with the bare interaction. The real issue, of course, is the convergence properties of the self-energy expansion in the bare versus screened interaction and this is best addressed computationally.

Interestingly, the GF2 approximation is also ammenable to the static approximation [set the brackets equal to

FIG. 1. The first two terms in Hedin's exact series expanded to consistent order in the screened interaction (wiggly line.) The GF2 approximation includes only bare interactions (dashed lines) in the $GWGW$ term.

zero in Eq. (2.19)] as are higher-level approximations such as the diagonal two-particle-hole Tamm-Dancoff approximation.[41] Unfortunately, there appears to be no particular advantage to this, because no simple linear response interpretation emerges.

This completes a rather detailed formal description of the COHSEX approximation. The approximation consists of two assumptions. The GW approximation is common in solid-state theory where "exchange diagrams" are known to be negligible in the high-density limit, but is likely to be regarded as suspicious by atomic and molecular physicists until proven otherwise. The static approximation is even more severe, but may be useful for outer valence ionization, among other things. These approximations have been more fully explored numerically and the results are given in Sec. III.

III. RESULTS AND DISCUSSION

In this section, we report the results of numerical calculations of outer valence ionization potentials and generalized overlaps for small molecules using the COHSEX2 and related approximations.

A. Computational details

A second-order Green-function program was written to use the eigenvectors, eigenvalues, and integrals produced by performing restricted Roothaan-Hartree-Fock (which we shall denote SCF) with the GAUSSIAN76 package.[42] The required atomic orbital to molecular orbital two-electron integral transformation was built directly into the Green-function program so that only those integrals actually needed were transformed. All terms in the COHSEX2, $GW2$, GF2, etc., expansions were retained, in contrast to the not uncommon practice of freezing out core orbitals or high-lying virtuals or using a truncation limit on the size of the terms retained. Debugging was facilitated by comparison with a "perturbation corrections to Koopmans's theorem program."[43–48]

Dyson's quasiparticle equation can become somewhat expensive to solve unless a few additional approximations are used. The self-energy is truely small for outer valence ionization and the first-order perturbation theory

$$\omega = \varepsilon_k + \Sigma_{kk}(\omega) , \quad (3.1)$$

$$\langle r|\phi \rangle = \delta_{rk} + \frac{\Sigma_{rk}(\omega)}{\varepsilon_k - \varepsilon_r} \quad (3.2)$$

gives results which differ only slightly from full diagonalization of the QPE Hamiltonian while at the same time avoiding the need to ever construct the whole QPE Hamiltonian matrix. (Minor modifications are required to allow for the case of degeneracies due to symmetry.) In particular, the "diagonal approximation" [Eq. (3.1)] leads to errors of less than 0.1 eV in the calculation of outer valence IP's. (See also Refs. 49 and 50.) A somewhat more severe, but still good approximation, is the "quasiparticle approximation" in which the self-energy is evaluated at $\omega = \varepsilon_k$ in Eqs. (3.1) and (3.2). The diagonal quasiparticle GF2 calculation is, in fact, identical to a second-
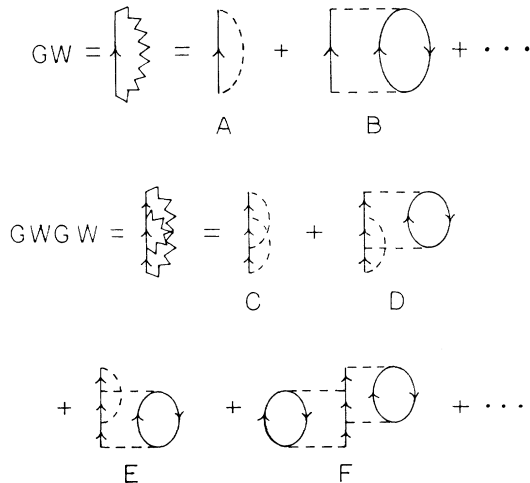
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order perturbation corrections to Koopmans's theorem calculation.[51-53] Spectroscopic factors were evaluated in the diagonal approximation

$$S_k^{-1}(\omega) = 1 - \frac{\partial \Sigma_{kk}(\omega)}{\partial \omega} \qquad (3.3)$$

and these can be used to correct the quasiparticle approximation by the Newton-Raphson formulas

$$\omega_1 = \varepsilon_k + \Sigma_{kk}(\omega_0) ,$$

$$\omega_2 = \omega_0 + S_k(\omega_0)(\omega_1 - \omega_0) , \qquad (3.4)$$

with shifts of a few tenths of an eV being typical. However, Newton-Raphson corrections have not been made in any of the tabulated numbers except where otherwise specified.

Calculations were performed for nine small molecules for vertical ionization at geometries (listed in Table I) close to the experimental geometries. All but one of these calculations used the 4-31G basis set[54] internal to GAUSSIAN76. Based on previous work,[44] a double-ζ quality basis set is expected to be able to yield IP's within about 0.5 eV of experiment when a third-order or higher-level approximation is used. The 4-31G basis set gives results somewhat similar to a double-ζ basis set when calculating IP's, though the IP's seem to be lower.[48] To obtain an indication of basis-set effects and to calculate meaningful generalized overlaps, a more elaborate basis set was used for water. This was the $[7s4p1d/3s1p]$ basis constructed using contraction 10 in Table 3, contraction 5 in Table 8, and contraction 5 in Table 9 of Ref. 55 and then adding a set of five d functions with exponent 0.80 on the oxygen and a set of p functions with exponent 1.00 on the hydrogen atoms. We will also refer to the very high-quality calculation of Bawagan, Brion, Davidson, and Feller[56] for H_2O using what we shall term the 109GTO (for Gaussian-type orbital) basis set. Self-consistent field-restricted Roothaan-Hartree-Fock total energies and dipole moments are listed in Table II.

B. Ionization potentials

Outer valence vertical ionization potentials were calculated for the nine molecules and are compared with experiment in Tables III and IV. Deviations from experiment are shown in parentheses. Asterisks denote cases

TABLE II. SCF total energies and dipole moments.

	Total energy (a.u.)	Dipole moment (D)
H_2O	-75.9074	2.6082
H_2O^a	-76.0569	2.2542
H_2O^b	-76.0675	1.980
F_2	-198.4584	0.0
CO	-112.5524	0.6017
HOF	-174.5156	2.5586
HNO	-129.5778	2.3787
C_2H_2	-76.7109	0.0
trans-N_2H_2	-109.8104	0.0
H_2O_2	-150.5549	2.0460
CH_2O	-113.6911	3.0050

[a] $[7s4p1d/3s1p]$ basis set.
[b] 109GTO.

where the calculated order of ionization potentials (or their quasidegeneracy in the case of hydrogen peroxide) differs from experiment. The water results in Table III give some idea of the basis-set effects. Table V gives the water results with the Newton-Raphson correction. Koopmans's theorem typically gives IP's which are 1-2 eV *too high* and, not infrequently, orders them incorrectly. The "old standard" GF2 calculation does much better in ordering the IP's but typically gives IP's which are 1-2 eV *too low*. This is a symptom of the inconvenient oscillatory convergence of IP's when the self-energy is expanded order by order in the *bare* interaction.[50] The COHSEX2 approximation does much better, typically giving the first IP to within 0.5 eV of experiment and giving the correct order of ionization potentials. This seems a remarkable result given the apparent crudeness of the approximations described in Sec. 2, and so it is of special interest to examine the origin of this success. Specifically, is the success of the COHSEX2 approximation due to the *GW*2 approximation, the static approximation, or perhaps due to fortuitous cancellation of errors between the two?

As Tables III-V show, the *GW*2 approximation is significantly better than either Koopmans's theorem or the GF2 approximation. This is surprising when one considers the frequent reference to the GF2 approximation and the relative obscurity of the *GW*2 approximation in the atomic and molecular physics literature.

Since the COHSEX2 approximation is still signif-

TABLE I. Geometry, bond lengths and bond angles.

	Geometries		
H_2O	$R(OH) = 0.9572$ Å	$\angle(HOH) = 104.52°$	
F_2	$R(FF) = 1.418$ Å		
CO	$R(CO) = 1.128$ Å		
HOF	$R(OF) = 1.4422$ Å	$R(OH) = 0.9641$ Å	$\angle(HOF) = 97.26°$
HNO	$R(NO) = 1.212$ Å	$R(HN) = 1.063$ Å	$\angle(HNO) = 108.6°$
C_2H_2	$R(CC) = 1.203$ Å	$R(CH) = 1.061$ Å	Linear
trans-N_2H_2	$R(NN) = 1.2522$ Å	$R(NH) = 1.0285$ Å	$\angle(NNH) = 106.85°$ planar
H_2O_2	$R(OO) = 1.475$ Å	$R(OH) = 0.95$ Å	$\angle(OOH) = 94.8°$ $\angle(HOOH) = 111.5°$
CH_2O	$R(CO) = 1.2078$ Å	$R(CH) = 1.1161$ Å	$\angle(HCO) = 121.74°$ planar

icantly better than the $GW2$ approximation for at least the first IP, the static approximation is also significant. The static approximation is expected to work best near the center of the HOMO-LUMO gap, so it is of particular interest to test it in this energy region. Table VI compares the static and "gap" approximations for water, two different basis sets, and both the $GW2$ and GF2 methods. Although hardly obvious from the formulas, the static and "gap" approximations give IP's for water which differ by only about 0.5 eV, and tests on the other eight molecules give similar results. The two approximations might be called "close." This suggests that the static approximation should work best for the first IP and become successively worse as the IP's increase within a molecule, in agreement with the observed general trend (Tables III and IV). However, the magnitude of the self-energy (calculated IP less SCF orbital energy) is significantly different for the static and "gap" approximations.

Since the "gap" approximation invariably overestimates ionization potentials, the COHSEX approximation will generally overestimate the $GW2$ result (Tables III and IV). [This property of the "gap" approximation follows directly from Eq. (3.4) since $S_k < 1 \Longrightarrow \omega_2 - \mu < \omega_1 - \mu$.] The high quality of the first IP calculated via the COHSEX2 approximation appears to be due to a combination of the quality of the $GW2$ result and the artificial overestimate from the static approximation. It

is thus an artifact and one which is not helpful in calculating the other IP's. We consider this a problem, and so it is interesting to know if it can be corrected within the spirit of the COHSEX approximation. To this end, consider expanding the $GW2$ self-energy [Eq. (2.19)] in a Taylor's series about the center of the HOMO-LUMO gap and then making the static approximation in the analytic expression *for each coefficient*. The final answer may be expressed as

$$\Sigma(\mathbf{r},\mathbf{r}';\omega) = \delta(\mathbf{r}-\mathbf{r}')X_+(\mathbf{r},\mathbf{r}';\omega-\mu)$$
$$-\gamma(\mathbf{r},\mathbf{r}')W_p(\mathbf{r},\mathbf{r}';\omega-\mu) , \qquad (3.5)$$

which reduces to the COHSEX approximation in the limit $\omega = \mu$. Equation (3.5) is equivalent to Eq. (2.19) with the second term in each numerator discarded and the bracketed terms replaced with $\omega - \mu$. We have evaluated this up through the linear term in $\omega - \mu$ in Taylor's expansion and call this the "modified COHSEX" approximation. It is denoted M-COHSEX in Tables III and IV which show that the new approximation agrees rather more satisfactorily with the $GW2$ results, lending general support for the approximate identification of the static and "gap" approximations. This again involves some fortuitous cancellation of error due to the previously mentioned *overestimate* of the IP in the unmodified COHSEX approximation coupled with an *underestimate* of the

TABLE III. Outer valence vertical ionization potentials labeled by the hole formed in the zero-order picture. The $GW2$, M-COHSEX2, COHSEX2, and GF2 methods are described in the text. Deviations from the experimental values are given in parentheses. Asterisks denote an order reversal.

		Ionization potentials (eV)				
	Expt.	$GW2$	M-COHSEX2	COHSEX2	GF2	Koopmans's
H_2O	Ref. 61					
$1b_1$	12.61	11.72(−0.89)	11.58(−1.03)	12.28(−0.33)	10.55(−2.06)	13.59(+0.98)
$3a_1$	14.73	13.70(−1.03)	13.49(−1.24)	14.34(−0.39)	12.71(−2.02)	15.19(+0.46)
$1b_2$	18.55	18.62(+0.07)	18.26(−0.29)	19.42(+0.87)	17.99(−0.56)	19.25(+0.70)
H_2O[a]	Ref. 61					
$1b_1$	12.61	11.86(−0.75)	12.04(−0.57)	13.00(+0.39)	10.79(−1.82)	13.84(+1.23)
$3a_1$	14.73	14.18(−0.55)	14.14(−0.59)	15.37(+0.64)	13.17(−1.56)	15.86(+1.13)
$1b_2$	18.55	18.60(+0.05)	18.25(−0.30)	19.86(+1.31)	17.79(−0.76)	19.55(+1.00)
F_2	Ref. 62					
$1\pi_g$	15.83	15.27(−0.56)	14.74(−1.09)	15.75(−0.08)	13.33(−2.50)	18.16(+2.33)
$1\pi_u$	18.80	18.41(−0.39)	18.05(−0.75)	19.39(+0.59)	15.93(−2.87)	21.99(+3.19)*
$3\sigma_u$	21.0	20.41(−0.6)	19.81(−1.2)	21.87(+0.9)	19.92(−1.1)	19.93(−1.1)*
CO	Ref. 63, p. 34					
5σ	14.01	13.82(−0.19)	13.47(−0.54)	14.35(+0.34)	13.28(−0.73)	14.93(+0.92)
1π	16.91	16.63(−0.28)	16.16(−0.75)	17.67(+0.76)	16.18(−0.73)	17.67(+0.76)
4σ	19.72	18.63(−1.09)	17.49(−2.23)	19.54(−0.18)	16.87(−2.85)	21.61(+1.89)
HOF	Ref. 64					
$2a''$	13.0	12.49(−0.5)	12.07(−0.9)	12.95(−0.05)	10.90(−2.1)	14.95(+2.0)
$7a'$	14.8	14.55(−0.2)	14.00(−0.8)	15.21(+0.4)	13.14(−1.7)	16.41(+1.6)
$1a''$	16.0	16.30(+0.3)	15.87(−0.1)	17.19(+1.2)	14.06(−1.9)	19.56(+3.6)*
$6a'$		17.32	16.71	18.40	16.28	18.24*
$5a'$		18.72	18.19	19.71	17.15	20.92

[a]$[7s4p1d/3s1p]$ basis set.

TABLE IV. Outer valence vertical ionization potentials labeled by the hole formed in the zero-order picture. The $GW2$, M-COHSEX2, COHSEX2, and GF2 methods are described in the text. Deviations from the experimental values are given in parentheses. Asterisks denote an order reversal.

		Ionization potentials (eV)				
	Expt.	$GW2$	M-COHSEX2	COHSEX2	GF2	Koopmans's
HNO	Ref. 65					
$7a'$	10.29	10.07(-0.22)	9.66(-0.63)	10.35($+0.06$)	8.87(-1.42)	11.81($+1.52$)
$6a'$		15.63	14.98	16.59	14.15	17.85*
$1a''$		16.42	15.95	17.71	16.24*	16.15*
$5a'$		17.74	17.20	19.02	16.04*	20.23
C_2H_2	Ref. 63, pp. 190–193					
$1\pi_g$	11.40	11.20(-0.20)	11.13(-0.27)	12.16($+0.76$)	11.06(-0.34)	10.95(-0.45)
$3\sigma_g$	16.72	17.04($+0.32$)	15.92(-0.80)	17.70($+0.98$)	16.07(-0.65)	18.30($+1.58$)
$2\sigma_u$	18.75	18.72(-0.03)	17.30(-1.45)	19.42($+0.65$)	17.61(-1.14)	20.54($+1.79$)
trans-N_2H_2	Ref. 66					
$4a_g$	10.02	9.61(-0.41)	9.25(-0.77)	9.98(-0.04)	8.57(-1.45)	11.04($+1.02$)
$1a_u$	14.39	14.25(-0.14)	13.94(-0.45)	15.37($+0.98$)	14.03(-0.39)*	13.99(-0.40)
$3b_u$	15.03	14.92(-0.11)	14.39(-0.64)	15.82($+0.79$)	13.12(-1.91)*	17.44($+2.41$)
$3a_g$	16.9	17.32($+0.4$)	16.46(-0.4)	18.14($+0.8$)	16.49(-0.8)	17.18($+1.3$)
H_2O_2	Ref. 67					
$4b$	11.69	10.96(-0.73)	10.55(-1.14)	11.43(-0.26)	9.47(-2.22)	13.24($+1.55$)
$5a$	12.69	12.87($+0.18$)	12.38(-0.31)	13.55($+0.86$)	11.62(-1.07)	14.43($+1.74$)
$4a$	15.33	14.97(-0.36)	14.51(-0.82)	15.92($+0.59$)	13.75(-1.58)	16.40($+1.07$)
$3b$	17.40	17.40(0.00)	16.85(-0.55)	18.37($+0.97$)	16.19(-1.21)	18.88($+1.48$)*
$3a$	17.40	17.34(-0.06)	16.73(-0.67)	18.24($+0.84$)	15.84(-1.56)	19.56($+2.16$)*
H_2CO	Ref. 68					
$2b_1$	10.88	10.22(-0.66)	9.86(-1.02)	10.65(-0.23)	9.02(-1.86)	11.93($+1.05$)
$1b_2$	14.38	14.20(-0.18)	13.82(-0.56)	15.30($+0.92$)	13.80(-0.58)	14.49($+0.11$)
$5a_1$	16.00	15.41(-0.59)	14.47(-1.53)	16.21($+0.21$)	13.94(-2.06)	17.47($+1.47$)
$1b_1$	16.78	17.11($+0.33$)	16.83($+0.05$)	18.19($+1.41$)	15.88(-0.90)	19.03($+2.25$)
$3a_1$	21.8	21.58(-0.2)	20.50(-1.3)	22.47($+0.7$)	20.64(-1.2)	23.57($+1.8$)

spectroscopic factor in the M-COHSEX approximation as shown in Table VII [see also Eq. (3.4)]. It should be noted that the quantity $X_+(r,r',\omega)$ is part of most polarization propagator or linear response calculations and hence often accessible through theory.

We conclude that the success of the COHSEX2 approximation comes primarily from the $GW2$ approximation. However, the static approximation is an additional convenience because of its close physical association with static polarization effects on the charge density. This picture is evidently most applicable near the center of the HOMO-LUMO gap, but limited dynamical corrections are possible via Eq. (3.5) if $X_+(r,r';\omega)$ is known.

It is also interesting to note the connection between the generalized COHSEX approximation [Eq. (3.5)] and Sham and Kohn's 1966 density functional for the self-energy.[26] Sham and Kohn argued that the self-energy is a short-ranged kernal with a range on the order of the Thomas-Fermi wavelength for the local density. They conclude that for a system with slowly varying density,

$$\Sigma(r,r';\omega) \cong \Sigma_h[r-r';\omega-\mu+\mu_h(\rho(r_0));\rho(r_0)] ,\quad (3.6)$$

where r_0 is the average of r and r', $\rho(r_0)$ is the charge density at r_0, μ is the chemical potential [essentially Eq.

(2.18) in the thermodynamic limit], and the subscript h refers to the homogeneous electron gas of density $\rho(r_0)$. Equation (3.6) follows directly from the generalized COHSEX approximation provided we assume (i) variations in $X_\pm(r,r';\omega)$ dominate variations in $\gamma(r,r')$ as a

TABLE V. Newton-Raphson corrected ionization potentials for water. The $GW2$, M-COHSEX2, and GF2 methods are described in the text. Deviations from experiment are given in parentheses.

		Ionization potentials (eV)		
	Expt.	$GW2$	M-COHSEX2	GF2
H_2O	Ref. 61			
$1b_1$	12.61	11.83(-0.78)	11.58(-1.03)	10.92(-1.69)
$3a_1$	14.73	13.79($+0.78$)	13.49(-1.24)	13.01(-1.72)
$1b_2$	18.55	18.86($+0.31$)	18.25(-0.29)	18.12(-0.43)
H_2O[a]	Ref. 61			
$1b_1$	12.61	12.05(-0.56)	12.04(-0.57)	11.19(-1.42)
$3a_1$	14.73	14.32(-0.41)	14.14(-0.59)	13.50(-1.23)
$1b_2$	18.55	18.67($+0.12$)	18.25(-0.30)	17.97(-0.58)

[a][$7s4p1d/3s1p$] basis set.

TABLE VI. Comparison of the static and "gap" approximations. Deviations from the SCF Koopmans's theorem result in parentheses.

| | | Ionization potentials (eV) | | | | |
| | | $GW2$ | | | $GF2$ | |
	Gap	Static	Difference	Gap	Static	Difference
H_2O						
$1b_1$	12.26(-1.33)	12.28(-1.31)	$+0.02$	11.40(-2.19)	11.42(-2.17)	$+0.02$
$3a_1$	14.28(-0.91)	14.34(-0.85)	$+0.06$	13.58(-1.61)	13.54(-1.65)	-0.04
$1b_2$	19.20(-0.05)	19.42($+0.17$)	$+0.22$	18.84(-0.41)	18.95(-0.30)	$+0.11$
H_2O[a]						
$1b_1$	12.54(-1.30)	13.00(-0.84)	$+0.46$	11.79(-2.05)	12.46(-1.38)	$+0.67$
$3a_1$	14.95(-0.91)	15.37(-0.52)	$+0.42$	14.31(-1.55)	14.78(-1.08)	$+0.47$
$1b_2$	19.40(-0.15)	19.86($+0.31$)	$+0.46$	19.01(-0.54)	19.46(-0.09)	$+0.45$

[a]$[7s4p\,1d\,/3s\,1p]$ basis set.

function of density and (ii)

$$X_\pm(\mathbf{r},\mathbf{r}';\omega)\cong X_h^\pm[\mathbf{r}-\mathbf{r}';\omega;\rho(\mathbf{r}_0)]\ . \tag{3.7}$$

Condition (i) is that the density matrix is slowly varying when the density is slowly varying. Condition (ii) is equivalent to assuming that the dynamical polarization depends only on the local density. These assumptions seem plausible for a *slowly* varying electron gas (but not for a small molecule).

C. Generalized overlaps

Scattering amplitudes and transition moments are a more interesting and demanding test of any approximation for the self-energy. For this reason, we also report results for the spherically averaged momentum distributions (MD's) of the outer valence generalized overlaps for water. The close relationship between such MD's and the scattering cross sections measured by electron momentum [formerly called $(e,2e)$] spectroscopy under certain kinematic conditions[57-59] has prompted many studies of this quantity at the Koopmans's picture (zero self-energy) level (usually referred to as the frozen orbital approximation). The insufficiency of this approximation has necessitated the inclusion of what amounts to a non-

zero self-energy for first row (nitrogen–fluorine) hydrides if good agreement with experiment is required.[59] As a result, high-quality generalized overlap MD's have been calculated for water[56] and appear as the 109GTO SCF and configuration interaction (CI) calculations referred to in the present paper. Comparison of MD's calculated using the COHSEX2 and related approximations with the 109GTO CI MD's provides an interesting test of the quality of these approximations for the off-diagonal elements of the self-energy [Eq. (3.2)].

The MD is calculated by integration of the Fourier transformed generalized overlap over the solid angle

$$\Pi(p)=\int |\phi(\mathbf{p})|^2 d\Omega\ ,$$
$$\phi(\mathbf{p})=(2\pi)^{-3/2}\int \phi(\mathbf{r})e^{i\mathbf{p}\cdot\mathbf{r}}d\mathbf{r}\ , \tag{3.8}$$

for the generalized overlap normalized to one. The MD's for the three outer valence generalized overlaps of water look very similar. They all have roughly the shape expected from the asymptotic position space behavior of an atomic p orbital,[60]

$$\Pi(p)\propto \frac{p^2}{(\zeta^2+p^2)^4}\ . \tag{3.9}$$

Changes in the MD's with different self-energy approxi-

TABLE VII. Spectroscopic factors for water. 109GTO refers to the CI result. $GW2$ (μ) refers to using the $GW2$ self-energy evaluated at the center of the HOMO-LUMO gap. This "gap" approximation and the $GW2$, M-COHSEX2, COHSEX2, and GF2 approximations are described in the text.

| | | | Spectroscopic factors | | | |
	109GTO	$GW2$	$GW2$ (μ)	M-COHSEX2	COHSEX2	GF2
H_2O	Ref. 56					
$1b_1$	0.869	0.936	0.968	0.916	1.000	0.879
$3a_1$	0.882	0.940	0.959	0.916	1.000	0.881
$1b_2$	0.888	0.956	0.956	0.925	1.000	0.899
H_2O[a]	Ref. 56					
$1b_1$	0.869	0.906	0.954	0.868	1.000	0.868
$3a_1$	0.882	0.912	0.942	0.873	1.000	0.875
$1b_2$	0.888	0.930	0.935	0.887	1.000	0.895

[a]$[7s4p\,1d\,/3s\,1p]$ basis set.

TABLE VIII. Heights of spherically averaged momentum distributions for generalized overlaps of water calculated using the $[7s4p1d/3s1p]$ basis set. For the overlap wave function normalized to unity. Deviations from the SCF result in parentheses. The 109GTO heights are roughly $\pm 0.1 \times 10^{-2}$ a.u. or better. The $[7s4p1d/3s1p]$ heights are known more accurately. Calculations were not performed in the M-COHSEX2 approximation (see text). $GW2$ (μ) refers to using the $GW2$ self-energy evaluated at the center of the HOMO-LUMO gap. This "gap" approximation and the $GW2$, COHSEX2, and GF2 approximations are described in the text.

| | Momentum distribution heights $(10^{-2}$ a.u.$)$ | | |
	$1b_2$	$3a_1$	$1b_1$
109 GTO SCF	6.28	6.43	6.13
109GTO CI	6.30(+0.02)	6.84(+0.41)	6.62(+0.49)
SCF	6.31	6.42	6.11
GF2	6.83(+0.52)	7.51(+1.09)	7.38(+1.27)
$GW2$	6.46(+0.15)	7.15(+0.73)	6.96(+0.85)
$GW2$ (μ)	6.42(+0.11)	6.84(+0.42)	6.64(+0.53)
COHSEX2	6.25(−0.06)	6.63(+0.21)	6.37(+0.26)

mations are manifested primarily in the magnitude of the maximum (i.e., height) of the curve.[34] MD heights calculated using the various approximations are given in Table VIII. Our calculations were performed using the $[7s4p1d/3s1d]$ basis set described earlier and this is expected to be adequate for our purposes. In particular, this basis set includes diffuse functions which are absent from the 4-31G set, but which are essential for the quantitative description of MD's.[60] The 109GTO and $[7s4p1d/3s1d]$ SCF MD's are nearly identical.

The heights in Table VIII show much the same trends already observed with the ionization potentials. In particular, the $GW2$ and COHSEX2 approximations gives significantly better results than does the GF2 approximation. However, the COHSEX2 approximation underestimates the MD heights by about as much as the $GW2$ approximation overestimates the heights, and the "gap" calculation [$GW2$ (μ)] and the COHSEX2 approximation give somewhat different heights. Nevertheless examination of the height corrections to the frozen orbital approximation (MD height minus the SCF MD height) in Table VIII and the calculated IP corrections to Koopmans's theorem in Table VI show that, although the magnitude of the self-energy appears to be significantly in error in the COHSEX approximation, it does remarkably well at reproducing trends. In the case of IP's, this was sufficient to correct the ordering of the IP's by introducing a correction in the right direction. In the case of MD's, the underlying physics of the COHSEX approximation predicts that the correction to the frozen orbital approximation will be most important for orbitals lying primarily in polarizable parts of molecules. This is consistent with what is observed in electron momentum spectroscopy studies.[59] It is also evident in the water results in Table VIII once it is recognized that the $1b_1$ and $3a_1$ orbitals correspond to the lone pairs lying in the outer more polarizable portion of the molecule, while the $1b_2$ orbital is a bonding orbital located in the inner less polarizable part of the molecule.[60]

IV. CONCLUSION

Hedin's Coulomb-hole and screened-exchange approximation has been considered for application to small mole-

cules. Mathematically, the COHSEX approximation is an approximation for the self-energy which results from applying the static approximation to the GW approximation. Physically, the COHSEX approximation is a Hartree-Fock-like approximation which incorporates polarization but not dynamical effects (especially not inner-valence poles or multichannel effects). The primary computational advantage of the COHSEX approximation is that no summations over virtual orbitals are required once the static polarization is known. Since the polarization effects arise from the linear response of the charge density to an external local potential, the COHSEX approximation is formally a density-functional approximation. Moreover, the static polarizabilities can be calculated from the (ground-state) Kohn-Sham density-functional theory.[23,24] When combined with the COHSEX formalism, this would provide a (nonlocal) density functional for the self-energy and place the COHSEX approximation firmly in its role intermediate between the conventional Green-function and density-functional approaches to the self-energy. Obviously, one limit of the accuracy of a combined density-functional COHSEX approximation is the quality of the COHSEX approximation itself.

This paper has assessed the quality of the COHSEX approximation (without further density-functional approximations) for the calculation of outer valence ionization potentials and generalized overlaps for small molecules. Although several approximations were used (e.g., the G^0W approximation, and evaluating W only to second order in the bare interaction), we expect our conclusions to generalize to more elaborate treatments. Our numerical examples suggest that the COHSEX2 approximation is superior to Koopmans's theorem and is often superior to the popular full second-order approximation (GF2). In fact, the COHSEX2 approximation for small molecules is rather similar in quality to the COHSEX approximation for solids. It provides a rough semiquantitative and physically interpretable approximation for the self-energy adequate for obtaining the correct order of ionization potentials in small molecules and correct trends in generalized overlap spherically averaged momentum distributions. The success of the COHSEX2 approximation for molecules has been traced to

significant improvements in the GF2 approximation when the exchange diagram is neglected ($GW2$ approximation). The inclusion of the exchange diagram is equivalent to an inconsistent mixing of the screened interaction in the GW approximation with the bare interaction in the $GWGW$ term of Hedin's exact expansion. Thus, the GF2 approximation should overestimate the $GWGW$ term. The COHSEX2 approximation is only a crude approximation for the $GW2$ self-energy, but is still superior to the GF2 self-energy. The static approximation provides only a very rough approximation to the self-energy at the center of the HOMO-LUMO gap but this identification can be extended to yield a generalized COHSEX approximation [Eq. (3.5)] which is a significant improvement over the conventional COHSEX approximation when used in a linearized form. The generalized COHSEX approximation appears consistent with the classic result of Sham and Kohn[26] in the limit of a slowly varying electron gas. Several opportunities arise in ionization potential applications for fortuitous cancellation of errors. This does not appear to be true when applied to the calculation of generalized overlaps, but nevertheless generalized overlap spherically averaged momentum distributions calculated with the COHSEX2 and related approximations reflect most of the other characteristics observed in the ionization potential calculations. A particularly interesting implication of the COHSEX approximation is the prediction that orbitals lying in polarizable regions of molecules should have generalized overlaps which differ more significantly from SCF orbitals than would orbitals lying in less polarizable regions. This is very much in line with previous empirical conclusions based upon electron momentum spectroscopy measurements.

We conclude that the limit of accuracy of a COHSEX-based density-functional approximation for the self-energy is likely to be significantly better than both Koopmans's theorem or the GF2 approximation. Numerically, we find the COHSEX2 approximation to be particularly good for the first IP while modifications based upon the $GW2$ approximation are recommended for the other outer valence IP's. At the same time, a COHSEX-based density-functional approximation for the self-energy is expected to be inferior to more sophisticated Green-function approximations.

ACKNOWLEDGMENTS

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