Simplified Green-function approximations: Further assessment of a polarization model for second-order calculation of outer-valence ionization potentials in molecules

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Ab initio methods for calculating the binding-energy spectra of large molecules have traditionally been restricted to primarily either Koopmans's theorem or the density-functional transition-orbital method. The limitations of the former are well known, and the density-functional "band-gap problem" has led to a further realization of intrinsic difficulties with the latter. An increasingly popular alternative to these two methods is to seek a simple approximation for the Green-function self-energy. The Green-function self-energy is the optical potential seen by a scattering particle (hole). As such, the dominant many-body effects contributing to the self-energy result from polarization of the charge density at energies below the first excitation energy of the target molecule (quasiparticle regime), as well as excitations of the target at higher energies. The physical importance of polarization effects is apparent in Hedin's *GW* approximation, which treats the self-energy as a product of the Green function (G) and a screened interaction (W) that can be calculated (essentially) from the time-dependent linear response of the charge density. In the present paper, we examine the contribution of polarization to the usual second-order Green-function (GF2) approximation with respect to the calculation of outer-valence ionization potentials in small molecules. A simplified version (GW2) of the GW approximation is found to be an acceptable substitute for the GF2 approximation, provided a self-interaction correction is included to prevent an electron from polarizing itself. Polarization effects are further analyzed using the Coulomb-hole and screened-exchange (COHSEX) and modified-COHSEX (M-COHSEX) approximations. A second-order version (M-COHSEX2) of the M-COHSEX approximation is used to examine the origin of the incorrect ordering by Koopmans's theorem of the first three ionization potentials of the nitrogen molecule in terms of static polarization and retardation effects. Finite-basis-set errors are also explored. Although higher-order Green-function approximations must be examined before drawing final conclusions, we believe that the present work provides preliminary evidence that *suitably modified* versions of time-dependent density-functional, dielectric-function-based self-energy approximations can be useful for molecules.

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I. INTRODUCTION

Density-functional theory (Appendix G of Ref. [1] contains a bibliography of important review articles) is an increasingly popular method for *ab initio* electronic-structure calculations on solids and large molecules where other *ab initio* methods would be impractical or prohibitively expensive. Modern treatments of density-functional theory are usually based upon key papers by Hohenberg and Kohn [2] and Kohn and Sham [3], which helped to give the earlier Thomas-Fermi theory (reviewed in Ref. [4]) and Slater's $X\alpha$ method (reviewed in Ref. [5]) a firm theoretical foundation. However, Sham and Kohn [6] were quick to point out that substantial modifications in existent density-functional methods would be required before they could be used to calculate transition properties such as the quasiparticle band spectra of solids. Despite numerical evidence to the contrary [7], some solid-state theorists hoped that ordinary (ground-state) Kohn-Sham density-functional theory could be made sufficiently accurate to calculate useful band gaps for semiconductors and insulators. The origin of the so-called "band-gap problem" was clarified by Perdew and Levy [8] and Sham and Schlüter [9] and was later shown to be severe even if the true Kohn-Sham exchange-correlation potential is used [10]. Similar difficulties are encountered in molecular calculations. Molecular transition properties include ionization potentials (IP's), electron affinities, and related transition moments and scattering cross sections. Although the first IP's and electron affinities can be obtained in principle by Slater's transition-orbital method [5,11] (or by taking differences of accurately calculated ground-state energies), there is no formal justification for applying this method to calculate higher IP's and electron affinities, and the transition orbital method is simply incapable of describing the complex many-body effects [12] seen in inner-valence ionization spectra. (See also Ref. [13] for an assessment of very high-quality Hartree-Fock-Kohn-Sham calculations for the first IP's and electron affinities of atoms through zinc.) Similar objections apply to calculating scattering cross sections and transition moments via density-functional methods. These difficulties point to the need for new *ab initio* methods for large molecules. The present paper focuses on simplified Green-function methods, especially those approximations which seem best suited for use in conjunction with density-functional methods.

The Green-function 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 [14(a)], scattering cross sections [14(b)], and ground-state properties [14(c)]. Although elaborate and accurate approximations for the self-energy are known [14], it is clear that less elaborate, less computationally intensive approximations are also useful. A variety of simplified self-energy approximations have been suggested, including approximations based upon the separation of correlation and relaxation effects [15] and approximations based upon approximate "antigraph" relations [16]. However, the most interesting approximations from the point of view of combining density-functional and Green-function methods are formulations developed for extended systems involving the linear response or polarization of the charge density. These comprise several related methods, including Hedin's GW and Coulomb-hole and screened-exchange (COHSEX) approximations [17,18], and may be collectively termed the "dielectric-function method" [19]. Although well entrenched in solid-state electronic-structure theory [17,18,20], they have only occasionally been applied to molecules using the Pariser-Par-Pople (PPP) semiempirical Hamiltonian [21–26] or PPP-like approximations in an *ab initio* framework [27,28]. Consequently, they are not yet well understood for *ab initio* calculations on molecules where finite volume effects [21,22], non-negligible self-interactions [29], and non-negligible exclusion-principle-violating diagrams [30] (to name a few effects not present in extended systems) may require the original theory to be modified.

In a previous study [31] (hereafter referred to as paper I), we presented what we believe to be the first *ab initio* assessment of the COHSEX and GW approximations for molecules, albeit using second-order approximations. The present paper is an elaboration on our previous work, focusing primarily on self-interaction and finite-basis-set errors left unexplored in paper I and including a more detailed discussion of how static polarization and retardation effects influence IP's. As in paper I, we restrict ourselves to the exploration of second-order approximations as applied to the calculation of outer-valence IP's in the belief that it is best to explore the polarization physics of the simplest Green-function approximation used in the molecular literature before considering higher-order approximations.

Although motivated by developments in density-functional theory, we emphasize that none of the results reported in paper I or the present paper include density-functional approximations. This is because we are not yet convinced that the dielectric-function method is well enough understood for molecules to warrant the incorporation of density-functional techniques at this time. However, since paper I and the present paper represent steps in that direction, it is appropriate to compare and contrast the dielectric method with other density-functional techniques. One important difference is that whereas conventional density-functional methods make a local exchange approximation, exchange is treated exactly in the dielectric-function method. Hence the method will suffer from most of the computational difficulties of Hartree-Fock calculations. This is certainly not a problem when starting from a Hartree-Fock-Kohn-Sham calculation in which the exchange is treated exactly (Ref. [1] pp. 183–186), but may appear undesirable when beginning from a conventional Kohn-Sham calculation because it is well known that finite-basis-set implementations of Kohn-Sham theory scale as the third power of the size of the basis set, while finite-basis-set Hartree-Fock calculations scale as the fourth power of the size of the basis set. It is therefore important to note that the pseudospectral approximation [32] reduces the difficulty of Hartree-Fock calculations to scaling as the third power of the size of the basis set. Simpler approximations, which can be construed as density functionals of the self-energy, have been reviewed in paper I. The dielectric method provides a more complicated *time-dependent* density-functional formalism which may be useful when simpler methods fail. (It should also be pointed out that a formal basis for time-dependent density-functional theory [33] is a relatively recent phenomenon and important fundamental questions are still being resolved [34]. Nevertheless, encouraging preliminary atomic and molecular calculations [35] have been made using the time-dependent local-density approximation (TDLDA) and these, together with condensed-matter applications, have been reviewed in Ref. [36].)

The remainder of this paper is divided as follows. The quasiparticle equation formalism, the GW, and further approximations are reviewed in Sec. II in an effort to keep the paper somewhat self-contained. Second-order approximations are introduced in Sec. III and then examined with respect to self-interaction and finite-basis-set errors, and the manner in which static polarization and retardation effects influence molecular IP's is discussed in some detail. Our conclusions are presented in Sec. IV.

Certain conventions are adhered to throughout this paper. Atomic units are used throughout unless otherwise specified, the symbol η is used (throughout) to denote the positive real infinitesimals frequently required in the Green-function method, and, for simplicity, we shall restrict ourselves to closed-shell molecules with wave functions in a definite spin state. Under these circumstances the Green function, density matrix, and the self-energy factor into spin α and spin β blocks whose spatial parts are identical. A superscript α will denote the spatial part of the spin α block. The total charge density is the sum of the spin α and spin β charge densities. A sum of the $(\alpha\alpha,\alpha\alpha)$-, the $(\alpha\alpha,\beta\beta)$-, the $(\beta\beta,\alpha\alpha)$-, and the $(\beta\beta,\beta\beta)$-spin blocks is taken to reduce the polarization propagator to a spin-free quantity (Ref. [37], pp. 110 and 111).

II. REVIEW

Some general formal theory is reviewed in this section before specializing to the second-order Green-function approximation in the Sec. III. This allows us to intro-

duce some basic concepts, establish notation, and keep the paper at least somewhat self-contained.

A. Quasiparticle equation

Dyson's quasiparticle equation [38] for a molecule M simultaneously describes vertical ionization

$$M \rightarrow M^+ + e^- , \tag{2.1}$$

where the wave functions for M and M^+ are, respectively, $\Psi^{(n)}$ and $\Psi_i^{(n-1)}$ and vertical electron attachment

$$M + e^- \rightarrow M^- , \tag{2.2}$$

where the wave function for M^- is $\Psi_i^{(n+1)}$, by a one-electron Schrödinger equation which may be written as

$$\left[\hat{h} + \int \frac{\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2\right]\psi(\mathbf{r}_1) + \int \left[\Sigma^\alpha(\mathbf{r}_1,\mathbf{r}_2;\omega) - \frac{\gamma^\alpha(\mathbf{r}_1,\mathbf{r}_2)}{r_{12}}\right]\psi(\mathbf{r}_2)d\mathbf{r}_2 = \omega\psi(\mathbf{r}_1) \tag{2.3}$$

for a closed-shell molecule, where h is the kinetic energy plus nuclear attraction part of the one-electron Hamiltonian. The eigenvalues of this pseudoeigenvalue problem are minus the vertical IP's and electron affinities of the molecule. The quasiparticle equation (2.3) differs from the Hartree-Fock equation in only two respects: the exact density ρ and exact (spin α) density matrix γ^α are used, and the self-energy is nonzero.

The primary focus in the present paper is upon the IP solutions. However, it is interesting to note that the negative electron affinity states of the quasiparticle equation are in fact continuum states. Thus the self-energy is the optical potential seen by a scattering electron [39,40]. As such, the physics of the self-energy is expected to be governed predominantly by polarization effects at energies below the first excitation energy of the target (quasiparticle regime), as well as by target excitations at higher energies. Similar reasoning applies to ionization ("hole scattering").

B. *GW* approximation

We now wish to make the relationship between the self-energy and polarization more concrete. This can be accomplished by examining the response of the self-energy to an arbitrary infinitesimal external local perturbation [17]. The polarizability arises naturally in this treatment as the response of the charge density. Hedin's *GW* approximation [17] is a lowest-order result which takes into account only the linear response of the charge density. The basic equations are reviewed below, and their interpretation is discussed. This discussion is aided by writing equations simultaneously in the time and energy representations. Terms neglected by the *GW* approximation include certain "exchange diagrams" as well as contributions from various (higher-order) combinations of linear and nonlinear responses of the charge density.

In the *GW* approximation, the spin-α self-energy is given by the simple product of the Green function (G) and the screened interaction (W) in the time and position representation

$$\Sigma_{GW}^\alpha(\mathbf{r},\mathbf{r}';\Delta t) = iG^\alpha(\mathbf{r},\mathbf{r}';\Delta t) \times \left[W(\mathbf{r},\mathbf{r}';\Delta t+\eta) - \frac{\delta(\Delta t+\eta)}{|\mathbf{r}-\mathbf{r}'|}\right] , \tag{2.4a}$$

$$\Sigma_{GW}^\alpha(\mathbf{r},\mathbf{r}';\omega) = \frac{i}{2\pi}\int e^{-i\eta\omega'} G^\alpha(\mathbf{r},\mathbf{r}';\omega-\omega') \times \left[W(\mathbf{r},\mathbf{r}';\omega') - \frac{1}{|\mathbf{r}-\mathbf{r}'|}\right] d\omega' . \tag{2.4b}$$

A physical interpretation of the *GW* self-energy stems from the screened interaction which is normally expressed in terms of the (causal) polarization propagator χ,

$$W(\mathbf{r},\mathbf{r}';\omega) = \frac{1}{|\mathbf{r}-\mathbf{r}'|} + \int \frac{1}{|\mathbf{r}-\mathbf{r}''|}\chi(\mathbf{r}'',\mathbf{r}''';\omega) \times \frac{1}{|\mathbf{r}'''-\mathbf{r}'|} d\mathbf{r}''d\mathbf{r}''' , \tag{2.5}$$

but which can be written in terms of the Fourier transform of the linear response of the charge density $\Delta\rho(\mathbf{r}'',\mathbf{r}';\Delta t)$ occurring at $\mathbf{r}''$ at time Δt after a unit charge impulse at $\mathbf{r}'$,

$$W(\mathbf{r},\mathbf{r}';\omega) = \frac{1}{|\mathbf{r}-\mathbf{r}'|} + \int \frac{1}{|\mathbf{r}-\mathbf{r}''|}\Delta\rho(\mathbf{r}'',\mathbf{r}';\omega)d\mathbf{r}'' . \tag{2.6}$$

[This involves replacing the causal polarization propagator with the retarded polarization propagator (Ref. [37], p. 174).]

The COHSEX approximation [17] is a further approximation in which the physical interpretation of the *GW* approximation is particularly clear. The COHSEX approximation results from the assumption that the screened interaction is sharply peaked at $\Delta t=0$ in the time representation. More precisely, the replacement

$$W(\mathbf{r},\mathbf{r}';\Delta t+\eta) - \frac{\delta(\Delta t+\eta)}{|\mathbf{r}-\mathbf{r}'|} \rightarrow \left[W(\mathbf{r},\mathbf{r}';\omega=0) - \frac{1}{|\mathbf{r}-\mathbf{r}'|}\right] \times \left[\frac{\delta(\Delta t-\eta)+\delta(\Delta t+\eta)}{2}\right] , \tag{2.7a}$$

$$\left[W(\mathbf{r},\mathbf{r}';\omega') - \frac{1}{|\mathbf{r}-\mathbf{r}'|}\right]e^{-i\omega\eta} \rightarrow \left[W(\mathbf{r},\mathbf{r}';\omega=0) - \frac{1}{|\mathbf{r}-\mathbf{r}'|}\right]\left[\frac{e^{i\omega'\eta}+e^{-i\omega'\eta}}{2}\right] \tag{2.7b}$$

gives

$$\Sigma^{\alpha}_{\text{COHSEX}}(\mathbf{r},\mathbf{r}';\omega)$$
$$=[\tfrac{1}{2}\delta(\mathbf{r}-\mathbf{r}')-\gamma^{\alpha}(\mathbf{r},\mathbf{r}')]\left[W(\mathbf{r},\mathbf{r}';\omega=0)-\frac{1}{|\mathbf{r}-\mathbf{r}'|}\right]$$
$$=\delta(\mathbf{r}-\mathbf{r}')\int\frac{\Delta\rho(\mathbf{r}'',\mathbf{r}';\omega=0)}{|\mathbf{r}''-\mathbf{r}|}d\mathbf{r}''$$
$$-\int\frac{\gamma^{\alpha}(\mathbf{r},\mathbf{r}')\Delta\rho(\mathbf{r}'',\mathbf{r}';\omega=0)}{|\mathbf{r}''-\mathbf{r}|}d\mathbf{r}'' \tag{2.8}$$

after some manipulation. The local term may be interpreted as a Coulomb hole. The nonlocal term represents screening of the exchange potential. By construction, the COHSEX approximation takes into account that part of the *GW* self-energy arising from instantaneous polarization effects. It is termed a *static* approximation because it only involves a knowledge of the time-independent linear response of the charge density $2\pi\Delta\rho(\mathbf{r},\mathbf{r}';\omega=0)$. The remaining parts of the *GW* self-energy, neglected by the COHSEX approximation, are due to time delays between when the polarization of the charge density by the perturbing electron (hole) takes place and when the potential due to that polarization is felt. These are termed *retardation* effects. A wave-function treatment of scattering [41] gives some additional physical insight into the *GW* approximation.

C. Modified COHSEX approximation

In paper I, we examined the possibility of further approximations on the *GW* approximations which only require a knowledge of the polarization at low energies. The main reason for doing this is that considerable computational simplifications result when the TDLDA linear-response calculations are restricted to only a few energies [35]. The obvious approach is to try the COHSEX approximation since this requires only the static response, but a better approach is to use an average energy approximation to obtain a generalized COHSEX approximation [31],

$$\Sigma^{\alpha}_{G\text{-COHSEX}}(\mathbf{r},\mathbf{r}';\omega)$$
$$=\delta(\mathbf{r}-\mathbf{r}')X(\mathbf{r},\mathbf{r}';\omega-\mu)$$
$$-\gamma^{\alpha}(\mathbf{r},\mathbf{r}')\left[W(\mathbf{r},\mathbf{r}';\omega-\mu)-\frac{1}{|\mathbf{r}-\mathbf{r}'|}\right], \tag{2.9}$$

where $X(\mathbf{r},\mathbf{r}';\omega)$ is the half of the (causal) polarization potential

$$W_p(\mathbf{r},\mathbf{r}';\omega)=W(\mathbf{r},\mathbf{r}';\omega)-\frac{1}{|\mathbf{r}-\mathbf{r}'|}\approx\int\frac{\Delta\rho(\mathbf{r}'',\mathbf{r}';\omega)}{|\mathbf{r}-\mathbf{r}''|}d\mathbf{r}'' \tag{2.10}$$

with poles in the lower half of the complex plane

$$W_p(\mathbf{r},\mathbf{r}',\omega)=X(\mathbf{r},\mathbf{r}';\omega)-X(\mathbf{r}',\mathbf{r};-\omega)\ , \tag{2.11}$$

and μ should be chosen far away from the poles of the self-energy as possible, say at the center of the HOMO-LUMO gap in molecular calculations or in the center of the band gap in solid-state calculations. (In the language of quantum chemistry, HOMO stands for the highest occupied molecular orbital and LUMO stands for the lowest unoccupied molecular orbital.) The *G*-COHSEX approximation works best at $\omega=\mu$. It fails completely as $\omega-\mu$ approaches the first excitation energy, but the modified COHSEX approximation

$$\Sigma^{\alpha}_{M\text{-COHSEX}}(\mathbf{r},\mathbf{r}'\omega)$$
$$=\Sigma^{\alpha}_{G\text{-COHSEX}}(\mathbf{r},\mathbf{r}';\mu)$$
$$+\left[\frac{\partial\Sigma^{\alpha}_{G\text{-COHSEX}}(\mathbf{r},\mathbf{r}';\omega)}{\partial\omega}\right]_{\omega=\mu}(\omega-\mu) \tag{2.12}$$

works reasonably well over a greater energy range and requires only a knowledge of the linear response in the neighborhood of $\omega=0$. Thus the *M*-COHSEX approximation provides a practical further simplification beyond the *GW* approximation.

III. SECOND-ORDER RESULTS

A. Second-order approximation

The general theory presented in Sec. II provides a conceptual framework for analyzing the polarization physics of the self-energy. Rather than attempting to apply this to the (unknown) exact self-energy, we have chosen to study the model problem defined by the *GF*2 approximation.

The *GF*2 (α-spin) self-energy matrix can be written in the basis of the Hartree-Fock canonical orbitals ϕ_i and their orbital energies ε_i as

$$\Sigma^{GF2}_{rs}(\omega)=\sum_{i,a,b}\frac{[2(sa;ib)(ra;ib)-(sb;ia)](ra;ib)(n_i\bar{n}_a\bar{n}_b+\bar{n}_i n_a n_b)}{\omega-\varepsilon_a+\varepsilon_i-\varepsilon_b}\ , \tag{3.1}$$

where we use the conventions that

$$(rs;pq)=\int\phi_r(\mathbf{r}_1)\phi_s(\mathbf{r}_1)\frac{1}{r_{12}}\phi_p(\mathbf{r}_2)\phi_q(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2\ , \tag{3.2}$$

$$\bar{n}_i=1-n_i\ , \tag{3.3}$$

and n_i takes the values 1 for an occupied orbital and 0 for a virtual orbital. This divides into the so-called "direct term"

$$\Sigma^{GW2}_{rs}(\omega)=\sum_{i,a,b}\frac{2(sa;ib)(ra;ib)(n_i\bar{n}_a\bar{n}_b+\bar{n}_i n_a n_b)}{(\omega-\varepsilon_a)+\varepsilon_i-\varepsilon_b} \tag{3.4}$$

and the remaining "exchange term." The direct term takes into account the same polarization physics embodied in the *GW* approximation. In fact, the direct term can be obtained from the *GW* approximation by making two additional approximations: (i) that the Green func-

tion G can be replaced by the Hartree-Fock Green function and (ii) that the polarization propagator can be replaced by the Hartree-Fock polarization propagator. It can also be thought of as the full GW approximation truncated to second-order in the fluctuation potential (paper I), hence the label $GW2$ approximation. Static polarization effects can be separated from retardation effects by setting the term in parentheses in the denominator equal to zero to obtain the COHSEX2 approximation. *In the limit of a complete basis set,* this becomes equivalent to Eq. (2.8) using the Hartree-Fock density matrix and linear response. Replacing the term in parentheses in the denominator with $(\omega-\mu)$ gives the G-COHSEX2 approximation and the M-COHSEX2 approximation is then simply obtained by taking the derivative [Eq. (2.12)].

Calculations were carried out to separate and assess the relative importance of the exchange term, polarization physics as manifested in the $GW2$ approximation, and static polarization effects as manifested in the COHSEX2 approximation. The M-COHSEX2 approximation was also examined to see the effects of a partial inclusion of retarded polarization effects. All calculations were carried out, as in paper I, using the diagonal quasiparticle approximation

$$\omega=\varepsilon_k+\Sigma_{k,k}(\varepsilon_k) \tag{3.5}$$

and our own second-order Green-function program which makes use of the eigenvectors, orbital energies, and electron repulsion integrals calculated by the GAUSSIAN76 [42] Roothaan-Hartree-Fock self-consistent-field (SCF) program. Since our interest is the polarization physics of the self-energy, without accompanying excitation effects, only IP's in the quasiparticle regime are considered (i.e., which are too low in energy to create excitation as well as ionization). This corresponds to ionization out of outer-valence orbitals in the molecules considered here.

Unfortunately the calculated $GW2$, COHSEX2, and M-COHSEX2 results reported in paper I inadvertantly omitted the factor of 2 in Eq. (3.4) [31]. Figure 1 shows a correlation plot of the (corrected) theoretical *Koopmans's defects* (i.e., calculated IP–Koopmans's theorem [43] IP) plotted versus the experimental Koopmans's defect using the numbers from Tables III and IV in paper I as well as the results of nitrogen molecule calculations with the 4-31G basis described later in the present paper. It is clear that neglecting the factor of 2 gives fortuitously good agreement between the $GW2$ approximation and experiment and that this agreement disappears with the correction.

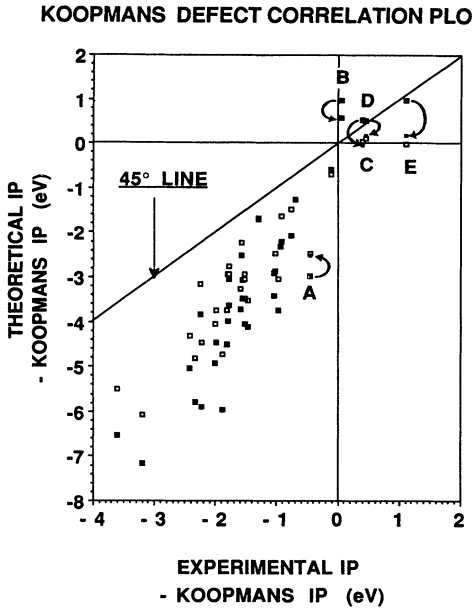

FIG. 1. Correlation plot of $GF2$, $GW2$, and SIC-$GW2$ theoretical Koopmans's defects vs experimental Koopmans's defects. (Koopmans's defect equals Green-function ionization potential minus Koopmans's theorem ionization potential.) The 45° line shows where perfect agreement between theory and experiment would fall. All theoretical calculations use the 4–31-G basis set and the experimental Koopmans's defect is referenced to the Koopmans's theorem ionization potential calculated using the 4–31-G basis set. The symbols are open open squares, $GF2$ Koopmans's defects; solid squares, $GW2$ Koopmans's defects; arrows and small solid squares indicate the effect of the SIC on the $GW2$ Koopmans's defects. Since the difference between the $GW2$ and SIC-$GW2$ results is usually small and to avoid unnecessary confusion, SIC-$GW2$ results have only been shown where the differences would be most noticeable and are labeled with capital letters in order from left to right: A, H_2O $(3a_1)^{-1}$; B, N_2 $(1\pi_u)^{-1}$; C, N_2H_2 $(1a_u)^{-1}$; D, C_2H_2 $(1\pi_u)^{-1}$; E, F_2 $(3\sigma_u)^{-1}$.

B. Self-interaction correction

The GW approximation was originally developed for application to the homogeneous electron gas (HEG) and, like other electron gas approximations [2,3,6], cannot be applied with impunity to small molecules [29,30]. We first show that this is so for two-electron molecules and then discuss corrections appropriate for molecules with two or more electrons.

The $GF2$ approximation is a very good approximation for two-electron atoms, capturing about 90–100 % of the Koopmans's defect if a sufficiently complete basis set is employed [44]. In contrast, a naive application of the $GW2$ approximation leads to disappointing results. One consequence of Eqs. (3.1) and (3.4) is that

$$\Sigma_{r,k}^{GW2}(\omega)=2\Sigma_{r,k}^{GF2}(\omega) \tag{3.6}$$

for a two-electron molecule with doubly occupied orbital k. It is easy to see, by taking the limit of a complete basis set and examining the COHSEX approximation [Eq. (2.8)], that the $GW2$ approximation has allowed each electron to polarize itself. This is precisely analogous to the self-interaction error [29] in applications of density-functional theory to small molecules. It does not arise in the case of the HEG only because the self-interaction of electrons in highly delocalized states is of negligible importance compared to interactions with all the other electrons.

Although this self-interaction error is unphysical and should be corrected, it is difficult to know the precise form of the self-interaction correction (SIC) except for two-electron molecules (see also Ref. [29]). Nevertheless, a reasonable approximate correction consists of replacing the polarization propagator in the *GW*2 approximation with the polarization propagator for the molecule with a hole in orbital k. Thus

$$\Sigma_{r,k}^{\text{SIC-}GW2}(\omega)=\sum_{i,a,b}\frac{(2-\delta_{i,k}-\delta_{b,k})(ka;ib)(ra;ib)(n_i\bar{n}_a\bar{n}_b+\bar{n}_i n_a n_b)}{(\omega-\varepsilon_a)+\varepsilon_i-\varepsilon_b} \tag{3.7}$$

for parent-molecule *occupied* orbitals k only, and similarly to obtain the SIC-COHSEX2 and SIC-*M*-COHSEX2 approximations. This gives

$$\Sigma_{r,k}^{\text{SIC-}GW2}(\omega)=\Sigma_{r,k}^{GF2}(\omega) \tag{3.8}$$

for two-electron molecules.

Self-interaction errors are expected to decrease as the number of electrons in the molecule increases. Indeed Fig. 1 shows that the *GW*2 self-energy is *on average* less than about 20% larger in magnitude than the *GF*2 self-energy for molecules with 10–18 electrons. Moreover, the ratio will go to 1 in the limit of the HEG. (The *GF*2 self-energy also diverges in this limit, but that does not concern us here.) Nevertheless, the ratio of *GW*2 to *GF*2 Koopmans's defects differs greatly from unity for IP's with positive Koopmans's defects. Our calculations indicate that the *GW*2 and SIC-GW2 Koopmans's defects are very similar, *except where the GW2 and GF2 approximations are markedly different.* In these cases, the inclusion of the self-interaction correction brings the (SIC-) *GW*2 and *GF*2 IP's into markedly better agreement. Since the difference between the *GW*2 and SIC-*GW*2 Koopmans's defects is usually small and to avoid unnecessary confusion, Fig. 1 shows SIC-*GW*2 Koopmans's defects *only* for those cases where the self-interaction correction was found to make the most noticeable difference.

An analogous problem was discussed by Kelly [30] in his early work applying many-body perturbation theory to atoms. He identified certain types of "exclusion-principle-violating" (EPV) diagrams as important in finite systems but negligible in extended systems (such as the HEG). One of Kelly's reasons for including EPV diagrams is reminiscent of the present need for a SIC, specifically (Ref. [30], p. 688) "since the effective potential may be changed by excitations." Since ionization can be thought of as analogous to an excitation which removes an electron and thereby changes the polarization potential, it is not surprising that adding EPV diagrams from the exchange term to the direct term gives a formula similar to the *GW*2 approximation

$$\Sigma_{r,s}^{GW2+\text{EPV}}(\omega)=\sum_{i,a,b}\frac{(2-\delta_{i,s}-\delta_{a,b}+\delta_{a,b}\delta_{i,s})(sa;ib)(ra;ib)(n_i\bar{n}_a\bar{n}_b+\bar{n}_i n_a n_b)}{(\omega-\varepsilon_a)+\varepsilon_i-\varepsilon_b}\,. \tag{3.9}$$

The SIC-*GW*2 and *GW*2+EPV approximations are in fact identical for two-electron molecules when $s=k$, the index of the single occupied orbital. The similarity is also apparent when a term-by-term comparison of the *GW*2 and *GF*2 approximations for the $(1\pi_u)^{-1}$ IP of the nitrogen molecule using the Slater-type orbital (STO)-3G basis set [45] and a simplified four-orbital model [46] which captures the most important physical features of the problem. The SIC-*GW*2 and *GW*2+EPV approximations are in fact identical in this situation when symmetry is taken into account. Moreover, the exchange term is dominated by a single EPV term which accounts for about 90% of the total exchange contribution. Since this exchange diagram also involves only two orbitals ($1\pi_u$ and $1\pi_g$), it is apparent that there is a strong similarity with the two-electron case.

C. Finite-basis-set errors

The results in Sec. III B and (most of the results in) paper I were calculated with the relatively small 4-31G basis set [47] and may contain finite-basis-set errors. Although it is well known that SCF calculations converge relatively quickly compared with post-SCF calculations as the size of the basis set is increased, it is also true that different types of post-SCF calculations converge at different rates with respect to the completeness of the basis set. This is a potential worry in the present case for two somewhat different reasons. The first reason is that the relative sizes of different self-energy terms may be basis-set dependent, so that conclusions drawn for small basis sets regarding the relative sizes of *GF*2, *GW*2, and SIC-*GW*2 self-energies might not hold for larger basis sets. The second reason is that the polarization interpretation of the COHSEX2 and related approximations embodied in Eqs. (2.8) and (2.9) is only strictly correct for a complete basis set. Clearly, finite-basis-set effects are of potential importance in separating fact from artifact in the physical interpretation of these approximations. We address the question of finite basis set errors by reporting the results of calculations of the first three IP's of molecular nitrogen with several basis sets of increasing completeness.

The calculations were carried out using the equilibrium bond length of 1.095 Å and several Gaussian-type basis sets. We use the general notation $[n_s s, n_p p, n_d d, \ldots]$ to

denote n_s contracted Gaussian-type orbitals (GTO's) functions, n_p contracted sets of GTO p functions, etc., per atom. A few basis sets have well-accepted names which we prefer to use. More specifically, we used the STO-3G ([2s1p], minimal) basis set [45], the 4–31G ([3s2p], split valence) basis set [47], the Huzinaga-Dunning double ξ ([4s3p], DZ (DZ stands for double S) basis set [48], the same supplemented with a set of 5d polarization functions with exponent $\alpha_d=0.8$ [4s3p1d], DZP (DZP stands for DZ plus polarization)), a [5s4p] basis set constructed using contraction 10 in Table 3 (note that the first two contractions were based upon the 1s orbital coefficients only) and contraction 8 in Table 8 of Ref. [49], the same supplemented with a set of 5d polarization functions with exponent $\alpha_d=0.75$ ([5s4p1d]), the [5s4p] basis supplemented with two sets of 5d polarization functions with exponents $\alpha_d=0.5$ and $\alpha_d=1.2$ ([5s4p2d]), and the [5s4p] basis supplemented with three sets of 5d polarization functions with exponents $\alpha_d=0.4$, 0.8, and 1.8 ([5s4p3d]). Total SCF energies for these basis sets are given in Table I.

The results of our calculations of the first three IP's are shown in Figs. 2–4. The most striking feature is that some of the post-SCF approximations converge at remarkably different rates even though the Koopmans's theorem (SCF) IP's are already nearly converged at the 4-31G basis-set level.

The convergence properties of the *GF*2, *GW*2, and SIC-*GW*2 approximations are remarkably similar. All are fairly rapidly convergent, but show a jump in their IP's with the introduction of polarization (i.e., d) functions. Most importantly the relationship between the three approximations is relatively independent of the size of the basis set, indicating that conclusions based upon calculations with small basis sets regarding the relative behavior of the three approximations also hold for larger basis sets.

On the other hand, the convergence rate of the COHSEX2 approximation is remarkably sensitive to the degree of completeness of the basis set and the presence of polarization functions in particular. This is important because the polarization interpretation of Eq. (2.8) is only valid in the limit of a complete basis set, so that any conclusions as to the relative importance of static versus retarded polarization effects should only be based upon calculations made using the largest ([5s4p3d]) basis set. Retarded polarization effects can be included in an approximate way by way of the *M*-COHSEX2 approximation. The nitrogen results presented here indicate much better agreement between the *GW*2 and *M*-COHSEX2 (or SIC-*GW*2 and SIC-*M*-COHSEX2) IP's, but convergence rates with respect to increasingly better basis sets seem to be roughly comparable to those of the COHSEX2 (SIC-COHSEX2) approximations although the IP's are shifted.

TABLE I. Total SCF energies for nitrogen molecule calculations. THe numerical Hartree-Fock value is from Ref. [50]. The asterisk denotes the interruption of monotonic increase of basis-set size.

Basis	Total SCF Energy (a.u.) Size	Energy
STO-3G	10	−107.495 1
4–31G	18	−108.753 88
DZ	20	−108.878 21
[5s4p]	34	−108.896 81
DZP	30*	−108.957 91
[5s4p1d]	44	−108.970 21
[5s4p2d]	54	−108.977 97
[5s4p3d]	64	−108.979 28
Numerical Hartree-Fock		−108.993 81

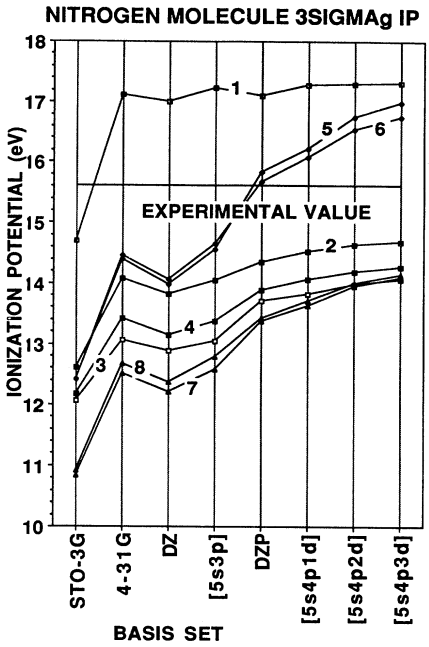

FIG. 2. Comparison of the convergence of various nitrogen molecule theoretical $(3\sigma_g)^{-1}$ ionization potential as a function of increasing basis set quality: curve 1, Koopmans's theorem; curve 2, *GF*2 approximation; curve 3, *GW*2 approximation; curve 4, SIC-*GW*2 approximation; curve 5, COHSEX2 approximation; curve 6, SIC-COHSEX2 approximation; curve 7, *M*-COHSEX2 approximation; curve 8, *M*-SIC-COHSEX2 approximation. The experimental ionization potential (Ref. [51]) is shown as a horizontal line.

D. Static polarization and retardation effects

The nitrogen molecule has come to be somewhat of a benchmark molecule for testing Green-function approximations because it is small enough to employ fairly complete basis sets and because Koopmans's theorem [43] orders the $(1\pi_u)^{-1}$ and $(3\sigma_g)^{-1}$ ionization potentials incorrectly. As Table II shows, the correct ordering can be achieved with the *GF*2 approximation provided a sufficiently complete basis set (including d functions) is employed. A qualitative explanation for this has been given previously [46] without reference to polarization effects. Our purpose is to discuss the same phenomenon from the point of view of static polarization and retardation effects in order to obtain a better understanding of the quasiparticle physics of this many-body process.

It is important to realize that the IP's predicted by the

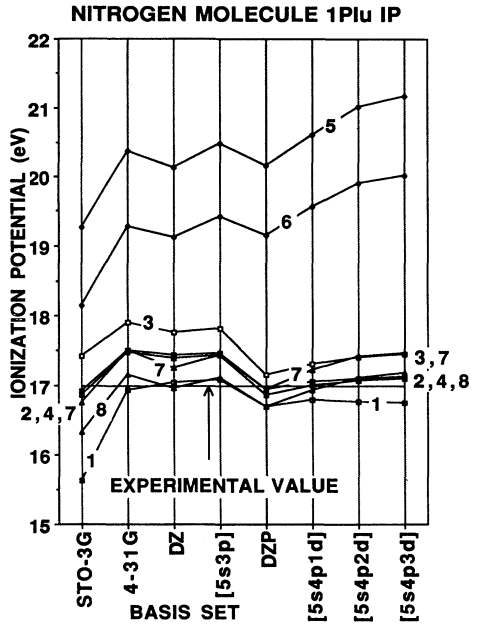

FIG. 3. Comparison of the convergence of various nitrogen molecule theoretical $(1\pi_u)^{-1}$ ionization potential as a function of increasing basis set quality: curve 1, Koopmans's theorem; curve 2, *GF*2 approximation; curve 3, *GW*2 approximation; curve 4, SIC-*GW*2 approximation; curve 5, COHSEX2 approximation; curve 6, SIC-COHSEX2 approximation; curve 7, *M*-COHSEX2 approximation; curve 8, *M*-SIC-COHSEX2 approximation. The experimental ionization potential (Ref. [51]) is shown as a horizontal line.

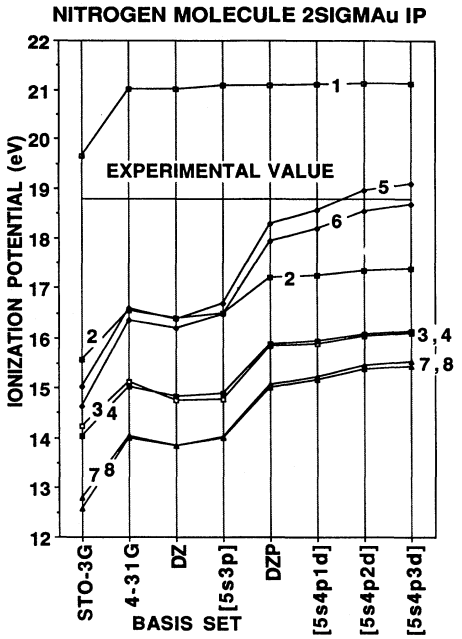

FIG. 4. Comparison of the convergence of various nitrogen molecule theoretical $(2\sigma_u)^{-1}$ ionization potential as a function of increasing basis set quality: curve 1, Koopmans's theorem; curve 2, *GF*2 approximation; curve 3, *GW*2 approximation; curve 4, SIC-*GW*2 approximation; curve 5, COHSEX2 approximation; curve 6, SIC-COHSEX2 approximation; curve 7, *M*-COHSEX2 approximation; curve 8, *M*-SIC-COHSEX2 approximation. The experimental ionization potential (Ref. [51]) is shown as a horizontal line.

*GF*2 approximation are not particularly good, even when large basis sets are used. As Fig. 1 shows, the *GF*2 self-energy correctly predicts global trends in Koopmans's defects but is roughly 2 times too large for the range of molecules and basis sets considered in this paper. Hence the second-order self-energies obtained by the COHSEX2, *M*-COHSEX2, *GW*2, and *GF*2 approximations have been *empirically corrected* by multiplying by 0.5 to obtain a more meaningful comparison with experiment (Table II). Before this correction, only the *GF*2 IP's are correctly ordered (but not particularly quantitative). After multiplying the self-energy by 0.5, *all* the Green-function approximations give the correct order of IP's.

TABLE II. Comparison of nitrogen molecule vertical ionization potentials calculated using the [5*s*4*p*3*d*] basis set. The experimental values are from Ref. [51]. The asterisk denotes order reversal.

Method	Vertical ionization potential (eV) $(3\sigma_g)^{-1}$	$(1\pi_u)^{-1}$	$(2\sigma_u)^{-1}$
Ab initio ionization potentials			
SCF	17.31*	16.75*	21.14
COHSEX2	16.98	21.17*	19.11*
M-COHSEX2	14.09	17.49*	15.53*
*GW*2	14.05	17.45*	16.10*
*GF*2	14.68	17.12	17.39
Empirically corrected *ab initio* ionization potentials			
0.5×COHSEX2	17.15	18.96	20.13
0.5×*M*-COHSEX2	15.70	17.12	18.34
0.5×*GW*2	15.68	17.10	18.62
0.5×*GF*2	16.00	16.94	19.27
Experiment	15.60	16.98	18.78

Bearing in mind that some empirical correction factor is needed at the second-order level of Green-function approximation, the most important feature to explain is the qualitative observation that the Koopmans's defects for the $(3\sigma_g)^{-1}$ and $(2\sigma_u)^{-1}$ IP's are much larger than for the $(1\pi_u)^{-1}$ IP. A wave-function–theoretic decomposition into correlation and relaxation effects shows that this feature is the result of a "pair relaxation" term which is unusually large because of the low-lying $1\pi_g$ resonance [46,52]. We wish to understand this feature at the level of the quasiparticle equation in terms of static and dynamic polarization effects.

As can be seen from Table II, the (empirically scaled) *M*-COHSEX2 approximation is the simplest approximation reflecting the experimentally observed behavior of the ionization potentials. Our discussion focuses on the *M*-COHSEX approximation. Equation (2.12) can be rewritten as

$$\Sigma_{q,q}^{M\text{-COHSEX}}(\omega)=\Sigma_{q,q}^{\text{COHSEX}}+(1-S_q^{-1})(\omega-\mu)\ , \quad (3.10)$$

where $0 \leq S_q, \leq 1$ (S_q is essentially the spectroscopic factor). The COHSEX term embodies static polarization effects. The second-term accounts for retardation effects. As Eq. (3.10) shows, retardation effects are manifestly positive for ionization solutions and manifestly negative for electron affinity solutions. Consequently, retardation effects always lower the value of calculated IP's and raise the value of calculated electron affinities. On the other hand, although the COHSEX2 approximation usually leads to smaller IP's than predicted by Koopmans's theorem (see the Appendix for a heuristic explanation), the opposite effect is also sometimes found to occur (paper I), and this is the case with the $(1\pi_u)^{-1}$ ionization in N_2. It is clear from Figs. 2–4 that the anomalously small $(1\pi_u)^{-1}$ Koopmans's defect in nitrogen results from a cancellation between static polarization and retardation effects. An interesting corollary is that the magnitude of correlation and relaxation effects is *not* simply related to the static polarizability alone of the molecule.

IV. CONCLUSION

Our objective in paper I and the present paper has been to explore simplified Green-function approximations which might be used to supplement density-functional calculations on large molecules. As in paper I, we have chosen to emphasize the physical meaning of our models wherever possible. A physical interpretation of the self-energy is provided by the recognition that it is the optical potential for a scattering particle (or hole) [31,39,40]. As such, the dominant many-body effects contributing to the self-energy are expected to result from polarization of the charge density at energies below the first excitation energy of the target (quasiparticle regime), as well as excitations of the target at higher energies. Our focus is on testing to what extent self-energy effects can be explained in terms of polarization effects.

We have reviewed Hedin's *GW* approximation which describes the interaction of an electron with a polarizable medium and made it the basis of a study of the polarization physics of the *GF*2 self-energy as applied to the calculation of molecular outer-valence (quasiparticle) ionization potentials. Our focus on the second-order level of approximation is a philosophical one in as much as we believe that it is best to explore the polarization physics of the simplest approximation before considering higher-order approximations. In particular, the *GF*2 self-energy divides into a direct term and an exchange term. The former is simply a second-order (*GW*2) approximation to the *GW* self-energy and represents the polarization part of the *GF*2 self-energy. We have shown that the remaining term helps to offset a self-interaction error in the *GW*2 self-energy which allows an electron to polarize itself. A self-interaction correction is introduced for the *GW*2 approximation, which leads to results that are essentially identical to those of the *GF*2 approximation for two-electron molecules but which is also important for some orbitals of molecules with more electrons. With this correction, a survey of several small molecules with the 4-31G basis set shows that the diagonal elements of the SIC-*GW*2 and *GF*2 self-energies are within about 25% of each other, so that the SIC-*GW*2 approximation provides a simple polarization interpretation of the *GF*2 self-energy. A careful examination of the first three IP's of the nitrogen molecule with respect to several basis sets shows that the relative sizes of the *GW*2, SIC-*GW*2, and *GF*2 self-energies is roughly independent of the size of the basis set.

For the basis sets and molecules considered in this paper, the *GF*2 approximation overestimates the size of the self-energy by a factor of about 2. When a semiempirical correction factor of 0.5 is included, the *GF*2 and *GW*2 approximations multiplied by 0.5 agree reasonably well with experiment for the first three IP's of molecular nitrogen. Consequently, it is possible to explore the origin of the incorrect ordering of the $(1\pi_u)^{-1}$ and $(3\sigma_g)^{-1}$ IP's of nitrogen by Koopmans's theorem in the context of polarization effects.

This is facilitated by the introduction of a modified Coulomb-hole and screened-exchange approximation, which aids in separating retardation effects from static polarization effects in the *GW* approximation. Although second-order versions of the Coulomb-hole and screened-exchange and *M*-COHSEX approximations were found to be more sensitive to the quality of the basis set than was the *GW*2 approximation, the *M*-COHSEX2 approximation appears to be a reasonable estimate of the *GW*2 self-energy. Examination of the *M*-COHSEX approximation shows that retardation effects will always tend to reduce the size of IP's, while static polarization effects can be of either sign (but usually also tend to reduce IP's). For the first three IP's of nitrogen, static and retarded polarization effects reinforce each other in the case of the $(2\sigma_u)^{-1}$ and $(3\sigma_g)^{-1}$ IP's and nearly cancel each other for the $(1\pi_u)^{-1}$ IP's. The net result (taking into account the semiempirical factor of 0.5) is the observed reordering of the Koopmans's theorem IP's.

We emphasize that the results in this paper apply only to the polarization physics of the *GF*2 approximation, which is the lowest-order self-energy approximation used in the molecular literature. Although the *GF*2 approximation can be a very good approximation (two-electron atoms [44]), the results in this paper show that it is primarily valuable for exploring the sign of and trends in self-energies. Nevertheless, although higher-order Green-function approximations must be examined before drawing final conclusions, we believe that the present work provides preliminary evidence that a *suitably modified* version of a time-dependent density-functional, dielectric-function-based self-energy approximation can be useful for molecules.

ACKNOWLEDGMENTS

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APPENDIX: HEURISTIC DERIVATION OF THE "EXPECTED" SIGN OF STATIC POLARIZATION EFFECTS

Although the COHSEX approximation can give rise to IP's which are either higher or lower than those predicted by Koopmans's theorem, a *lowering* of IP's is more frequently observed. At first thought, this may seem paradoxical, since the COHSEX approximation describes polarization effects which might be expected to enhance the screening between electrons, decrease their repulsion energy, and so increase their binding energy. The fallacy in this type of argument can best be seen by considering a simplified model of the homogeneous electron gas. In the Thomas-Fermi model of the HEG (Ref. [37], pp. 177 and 178)

$$W(\mathbf{r},\mathbf{r}';\omega=0)=\frac{e^{-q_{\mathrm{TF}}|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}\ , \tag{A1}$$

where q_{TF} is the Thomas-Fermi momentum. Static polarization effects act to reduce or screen the electron repulsion in this model. Moreover, we obtain

$$\Sigma^{\alpha}_{\mathrm{COHSEX}}(\mathbf{r},\mathbf{r}')=-\frac{q_{\mathrm{TF}}}{2}\delta(\mathbf{r}-\mathbf{r}')+q_{\mathrm{TF}}\gamma^{\alpha}(\mathbf{r},\mathbf{r}')+O(q_{\mathrm{TF}}^2) \tag{A2}$$

for the COHSEX self-energy; that is, the IP's are lowered by $q_{\mathrm{TF}}/2+O(q_{\mathrm{TF}}^2)$ and electron affinities are increased by $q_{\mathrm{TF}}/2+O(q_{\mathrm{TF}}^2)$ due to static polarization screening in this simple model.

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