



Green's function methods for calculating ionization potentials, electron affinities, and excitation energies

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Green's function (GF; electron propagator) methods represent a very useful set of tools for direct calculation of electron detachment (ionization potentials), electron attachment (electron affinities), excitation energies, electron transition probabilities, and other properties. The main idea of GF methods is that for description of various properties of a many-body system, one does not need to describe all the particles of the system but rather needs information about one or two particles belonging to the system. The corresponding required quantities are the one- and two-particle GFs. Within one- or two-particle GF methods, the energy difference between an initial state and a state with one additional or one less electron is calculated directly, thus eliminating errors due to inconsistent treatment of the initial and final states. © 2011 John Wiley & Sons, Ltd. *WIREs Comput Mol Sci* 2011 1 377–387 DOI: 10.1002/wcms.38

INTRODUCTION

The overview describes the basics of different Green's function (GF) approaches at a qualitative level. These approaches include two major types: the so-called quasiparticle (outer-valence Green's function, OVGF) approximation for both *ab initio* and semiempirical methods, and nondiagonal renormalized approaches (second- or third-order algebraic diagrammatic construction, ADC) for *ab initio* methods. Illustrative examples are given for some approaches.

Photoelectron (PE) spectroscopy is an extremely useful tool for studying the electronic structure of molecules. In order to interpret a PE spectrum, theoretical determination of the various ionization potentials (IPs) is necessary. Such determination can be obtained, e.g., using GF approach, which has been shown to yield good results.^{1,2} The GF formalism provides an alternative approach to the more common approaches, which are based on the wave function such as the equation-of-motion (EOM) and the linear response coupled cluster (CC) theories. These

wave function-based approaches can yield very accurate results, depending on the level of truncation in the CC expansion³; however, they are limited to fairly small molecules due to their high computational costs. Initially, the GF formalism has been developed and applied for the description of many-body systems in the context of quantum field theory.^{4,5} There are early attempts toward using GFs in quantum chemistry.^{6,7} In general, the basic idea of GF methods is that evaluation of the main characteristics of a many-body system does not require the description of all the system's particles but rather only information about one or two typical particles from the system. The corresponding theoretical quantities are the one- and two-particle GFs, respectively. As far as the electronic structure of molecules is concerned, the one-particle GF contains information regarding both the energies and the probabilities of an electron detachment/attachment processes. The two-particle GF, on the contrary, allows one to characterize excitation processes where the overall number of electrons in the system does not change. The conceptual advantage of GF methods lies in the fact that the interesting physical information is calculated directly without the need for separate calculations for the ground and ionic states. This, in turn, eliminates errors related to inconsistent treatment of the initial and final states.

One of the most significant achievements in the theoretical studies of PE spectra was the advent of

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DOI: 10.1002/wcms.38

OvGF method⁸ due to its computationally inexpensive technique for computing vertical one-electron ionization energies for outer-valence region. Another important step in this field is Schirmer's introduction of the ADC scheme.⁹ The approach removes the limitation of OvGF method to deal only with outer-valence region and allows to consider many-body effects in a systematic and consistent manner. The original ADC approach can be viewed as a reformulation of the perturbative diagrammatic expansions for GFs in terms of the Feynman–Goldstone diagrams.¹⁰ The more recent work of Schirmer et al.^{11,12} has demonstrated that ADC schemes can also be obtained within a framework of the more general concept of intermediate state representation. This allows ADC to use wave functions, which is the traditional language of quantum chemistry.^{13,14}

It has been shown that one-particle GF theory provides a systematic framework that improves the IPs and electron affinities (EAs) obtained within Koopman's theorem (KT) approximation, whereas two-particle GF is successfully applied to calculations of vertical excitation energies.

GREEN'S FUNCTIONS

The GF method is discussed in several general textbooks.^{10,15,16} Furthermore, a detailed discussion of the use of GF and other related methods in atomic and molecular physics is discussed in several reviews to which the reader is referred.^{1,2,8,9,17} Here, we only briefly present some of the main points of GF theory.

The GFs are defined as the N -electron ground-state expectation value of a time-ordered product of annihilation and creation operators. There is a hierarchy of the GFs determined by the number of considered particles. The most important ones for quantum chemistry are the one- and two-particle GFs. The simplest member of the hierarchy is the one-particle GF. The matrix of one-particle GF G (electron propagator) is defined with respect to a suitably chosen basis of one-particle states, which, in general, is a discrete set of Hartree–Fock (HF) orbitals by

$$G_{pq}(t, t') = -i \langle \Psi_0^N | \hat{T} c_p(t) c_q^\dagger(t') | \Psi_0^N \rangle, \quad (1)$$

where $|\Psi_0^N\rangle$ is the exact (close shell) nondegenerate ground state of the considered N -particle system, $c_q(t)$ and $c_q^\dagger(t)$ denote creation and annihilation operators for the one-particle state $|q\rangle$ in the Heisenberg representation and \hat{T} is Wick's time-ordering operator. The chemical properties contained in the GFs are most clearly expressed in the spectral representation of the

GFs, which can be obtained from Eq. (1) by means of Fourier transformation. For one-particle GF, the Fourier transformation is expressed by

$$G_{pq}(\omega) = \sum_n \frac{\langle \Psi_0 | c_p | \Psi_n^{N+1} \rangle \langle \Psi_n^{N+1} | c_q^\dagger | \Psi_0 \rangle}{\omega + E_0^N - E_n^{N+1} + i\eta} + \sum_m \frac{\langle \Psi_0 | c_q^\dagger | \Psi_m^{N-1} \rangle \langle \Psi_m^{N-1} | c_p | \Psi_0 \rangle}{\omega + E_m^{N-1} - E_0^N - i\eta}, \quad (2)$$

where $E_n^{N\pm 1}$ and $|\Psi_n^{N\pm 1}\rangle$ denote the energies and states of the $(N \pm 1)$ -particle systems, respectively, E_0^N is the ground-state energy, and a positive infinitesimal η is necessary to guarantee the convergence of the Fourier transformation. The physical significance of the one-particle GF derives from its relevance to the ionization and electron attachment spectrum, which is evident from Eq. (2). The first, $G^+(\omega)$, and second, $G^-(\omega)$, parts of $G(\omega)$ describe the attachment of an electron to the system and the elimination of an electron from the system, respectively. The ionization energies, $I_n = E_n^{N-1} - E_0^N$, and EAs, $A_n = E_0^N - E_n^{N+1}$, are derived from the pole positions of $G(\omega)$. The pole strength

$$P_n = |x_p^n|^2$$

is called the relative intensity because it provides a measure for the relative intensities of the states n , which derive their intensity from the same orbital p . The transition amplitude x_p^n is defined as

$$x_p^n = \begin{cases} \langle \Psi_0^N | c_p | \Psi_n^{N+1} \rangle & n \in \{N+1\} \\ \langle \Psi_n^{N-1} | c_p | \Psi_0^N \rangle & n \in \{N-1\} \end{cases} \quad (3)$$

The definition of GF operates only with accurate values (the electronic states and their energies), yet, for practical calculations, one has to introduce approximate schemes. The usual approximation procedure to evaluate the GF is by using a perturbation expansion. The poles of an unperturbed HF GF $G^0(\omega)$ are exactly the orbital energies, ε_n , as obtained from the KT approximation.¹⁸ In application of KT to close-shell system within the HF method, this theorem is commonly formulated in the particular form

$$I_n = -\varepsilon_n,$$

where I_n is Koopman's approximation to the n th IP, and ε_n is the respective eigenvalue of the HF equation

$$\hat{F} |\Psi_n\rangle = \varepsilon_n |\Psi_n\rangle.$$

Electron correlation and orbital relaxation are responsible for the quantitative failures of predictions based on KT for valence IPs. By introducing an effective energy-dependent one-particle potential $\Sigma(\omega)$, the

one-particle GF $G(\omega)$ can be derived from the unperturbed free GF $G^0(\omega)$ via the Dyson equation:¹⁹

$$G(\omega) = G^0(\omega) + G^0(\omega)\Sigma(\omega)G(\omega) \quad (4)$$

Here, the effective potential $\Sigma(\omega)$ (also called self-energy) on the basis of HF spin orbitals includes all relaxation and correlation corrections. The Dyson Eq. (4) plays a central role in the GF theory and the reader is thus referred to the discussion regarding Dyson equation and self-energy in configuration interaction representation, which is more familiar to the chemists.²⁰

OVGF METHOD

Often we are not interested in the full ionization spectrum, but only in the few IPs of outer-valence electrons, which characterize the molecule and provide direct information regarding their chemical bonding. The IPs assignment of the outer-valence electrons of a molecule is essential toward interpreting its PE spectrum. The simplest GF approximation, which takes into account only the outer-valence region is the OVGF method. This method was developed by Cederbaum and coworkers^{2,8} in the late 70s as a rather computationally inexpensive technique for computing vertical one-electron ionization energies. The method employs a finite expansion for the self-energy $\Sigma(\omega)$. It is based on the third-order expansion of the self-energy and includes higher order contributions by a normalization procedure. It has been shown² that in OVGF method, one may neglect off-diagonal matrix elements of the self-energy operator and use the $G(\omega)$ in its diagonal form $G_{pp}(\omega)$. This leads to the diagonal or quasiparticle approximation. Once the self-energy part has been calculated, the relevant pole of the GF is determined as a root of the Dyson equation. In OVGF method, the final equation for the self-energy is expressed by

$$\Sigma(\omega) \approx \Sigma^{(2)}(\omega) + (1 + A)^{-1}\Sigma^{(3)}(\omega), \quad (5)$$

where A in Eq. (5) actually depends on ω , but in the OVGF method where we are interested in energies ω far away from the poles of the self-energy, we may consider A to be a constant. Equation (5) involves calculation of the second- [$\Sigma^{(2)}(\omega)$] and third-order [$\Sigma^{(3)}(\omega)$] terms of the self-energy part, whereas A is an approximation to fourth and higher orders. Correlation corrections to ε_p are determined by iterating the equation,

$$\omega = \varepsilon_p + \Sigma_{pp}(\omega).$$

The explicit working equations for the second and third orders as well as for the parameter A can be found elsewhere.^{2,8} The OVGF method is a very practical and easy to handle method but also has some shortcomings. Interpretation of the ionization spectra in the OVGF method is based on the quasiparticle picture of ionization, which assumes a full correspondence between the PE line and the one-hole ionization state. However, it is well known^{2,21} that sufficiently strong relaxation and correlation effects in the cation yield an important dispersion of photoionization intensity from main line to many satellites of low intensity. This phenomenon is known as the breakdown of the orbital picture of ionization.²¹ It was pointed out by Deleuze²² that OVGF pole strengths smaller than ~ 0.85 very systematically foretell such breakdown. So far, the OVGF method, in general, is restricted to pole strength values between 0.85 and 1.0, indicating that the description via KT is qualitatively valid. The OVGF scheme is only applicable to ranges of electron binding energies where the self-energy is a smooth function and can be properly described by a finite expansion supplemented by a simple geometric approximation for the higher order terms. This depiction breaks down when entering those energy regions where the self-energy has poles related to electronically excited configurations of the cations (shake-up bands).²¹ For large saturated compounds, such as polycyclic aromatic hydrocarbons, the OVGF approach is most generally applicable to deep inner-valence levels (up to ~ 22 eV,²³), provided the computed OVGF pole strengths remain larger than ~ 0.85 .²⁴ On the contrary, both the outer-valence σ - and π -bands of large conjugated molecules are known to be subject to severe contaminations by shake-up lines, which in this case can be found at binding energies of ~ 8 eV.^{22,24} Finally, it is also difficult to systematically improve the method by extension to the next orders.

In 1996, Ortiz²⁵ developed an approximation known as a partial third-order quasiparticle theory (P3), which aimed at further simplifying the OVGF method. In his approach, several terms of $\Sigma^{(3)}(\omega)$ as well as the A factor are omitted from the calculations. The OVGF method requires ov^4 scaling [where o and v are the number of occupied and virtual molecular orbitals (MOs), respectively], whereas P3 calculations scale as o^2v^3 . Normally, in an *ab initio* calculation, the number of virtual MOs is much larger than that of occupied MOs, and therefore this reduction is quite significant. Ionization energy determined in P3 method has an average error of 0.2 eV for the small set of closed-shell molecules.²⁵ The working equation as well as the comparison of P3 method with other

quasiparticle approximations can be found elsewhere.²⁵ In 2005, Ortiz reported²⁶ a renormalization extension of the P3 self-energy (P3+ approach), which was successfully applied to the calculations of PE spectra of anions. Recently, Ortiz and coworkers²⁷ have suggested a new approach, which combined second-order electron propagator approximation with translation operator method. This new transition operator second order electron propagator (TOEP2) method scales only as ov^2 . The memory and calculation advantages are procured at the price of repeating TOEP2 calculations for each electron binding energy of interest. Because of its low scaling requirements, TOEP2 method may be very useful for the treatment of large biological systems. Although TOEP2 is outperformed by the P3 and OVGf methods in many applications of large molecules, it may be useful for assigning of the respective spectra. Both OVGf and P3 methods are implemented in Gaussian09 program package.²⁸

ADC METHOD

Unfortunately, methods based on low-order, perturbative corrections to diagonal elements of the self-energy matrix should, in general, not be applied to inner-valence ionization energies where higher excited configurations play a role and the one-electron picture collapses. In this case, one has to devise approximations that would be derived as infinite partial summation of the perturbation series. For this purpose, a set of methods that permits nonperturbative coupling between hole (h), particle (p), 2h-p, and 2p-h operators has emerged. One of the most practical and systematic ways of constructing such type of approximations is the method of the ADC introduced by Schirmer.⁹ The ADC approach sets out from the following nondiagonal representation,

$$\mathbf{G}^-(\omega) = \mathbf{f}^\dagger(\omega - \mathbf{K} - \mathbf{C})^{-1}\mathbf{f}, \quad (6)$$

where \mathbf{C} is an effective interaction Hermitian matrix, \mathbf{K} is the diagonal matrix of zeroth-order ionization energies, and \mathbf{f} is the effective transition moment. Equation (6) is obtained by inserting to the second term of Eq. (2) a complete set of so-called intermediate states $|\tilde{\Psi}_j^{N-1}\rangle$. These intermediate states can be constructed by a systematic procedure starting from the electronic ground state $|\Psi_0^N\rangle$.¹¹⁻¹⁴ We note with this respect that this treatment is entirely analogous for the both $[\mathbf{G}^-(\omega)$ and $\mathbf{G}^+(\omega)]$ terms. The ionization energies $\Omega_n = E_n - E_0$ can be obtained from the solution of the secular equation

$$(\mathbf{K} + \mathbf{C})\mathbf{Y} = \mathbf{Y}\boldsymbol{\Omega}, \mathbf{Y}^\dagger\mathbf{Y} = 1,$$

where \mathbf{Y} denotes the matrix of eigenvectors with the following components

$$Y_{jn} = \langle \tilde{\Psi}_j^{N-1} | \Psi_n^{N-1} \rangle.$$

This matrix relates to the transition amplitude define in Eq. (3) by

$$\mathbf{x} = \mathbf{Y}^\dagger\mathbf{f}.$$

In the ADC method, the approximate schemes are constructed by expanding the matrices \mathbf{K} , \mathbf{C} , and \mathbf{f} into a perturbation series. This method opens a highly systematic way for infinite partial summations for the self-energy matrix complete through a finite (n th) order of perturbation theory for formulation of approximations to arbitrary GFs. A thorough calibration of the accuracy of the most advanced ADC(3) method with respect to full Configuration Interaction (CI) and CC results for various small molecules is described by Schirmer and coworkers.²⁹ Only the low energy part of the PE spectrum can be correctly described based on the one-electron picture of ionization as obtained in the simpler OVGf approach. Therefore, applying of ADC(n) schemes in these cases is essential.

The equations for the ADC method are too complicated to be presented in the overview and the reader is referred to the original works of Schirmer et al.^{9,30} Explicit working equations of the ADC scheme for closed-shell systems are available elsewhere.^{2,8,30} ADC(3) method is implemented in the code³¹ developed in Heidelberg University, which can be linked to several quantum chemistry programs. It is available as well in the code developed by Ortiz and coworkers,³² which can be linked to the Gaussian09 program.

Most of the methods in the formalism of electron propagators use the Dyson Eq. (4). One peculiar and important feature of the Dyson equation is the coupling between the $(N - 1)$ -particle (ionization) and $(N + 1)$ -particle (electron affinity) configurations. This coupling, in general, cannot be neglected, even when one is interested solely in ionization spectrum. As was shown by Deleuze et al.,³³ an improper truncation in the many-body expansion of self-energy part $\Sigma(\infty)$ or the related one-particle GF $G(\omega)$ can yield a slight violation of the exact number of particles due to the coupling between the $N + 1$ and $N - 1$ states. This may result in a logarithmic divergence of the $\Sigma(\infty)$ as the system size increases.³³ This observation was one of the important motivations to formulate the non-Dyson ADC approximation for electron propagator, which was developed by Schirmer and coworkers.^{34,35} The approach successfully devises a formalism in which the ionization and affinity parts are analytically decoupled from the beginning,

so that the affinity evaluation is skipped from the ionization calculations. The main advantage of the non-Dyson ADC(n) methods [nD-ADC(n)] is that this scheme treats the electron ionization and attachment separately from each other, thus considerably reducing the computational costs compared with the usual Dyson-based ADC(n) methods. A comparison of the non-Dyson and Dyson ADC(3) calculations with experimental data and full CI results for a set of small molecules was presented in the work of Trofimov and Schirmer.³⁵ An efficient computer implementation of this approach was reported recently.³⁶

The next member of the hierarchy is the two-particle GF (polarization propagator). The Fourier transformation of the two-particle GF has the following spectral representation

$$\begin{aligned} \Pi_{pq,rs}(\omega) = & \sum_{n \neq 0} \frac{\langle \Psi_0 | c_q^\dagger c_p | \Psi_n \rangle \langle \Psi_n | c_r^\dagger c_s | \Psi_0 \rangle}{\omega + E_0^N - E_n^N + i\eta} \\ & + \sum_{n \neq 0} \frac{\langle \Psi_0 | c_r^\dagger c_s | \Psi_n \rangle \langle \Psi_n | c_q^\dagger c_p | \Psi_0 \rangle}{-\omega + E_0^N - E_n^N + i\eta}. \quad (7) \end{aligned}$$

According to Eq. (7), the vertical excitation energies $\Delta E_n = E_n - E_0$ are given by the poles of spectral representation, $\Pi_{pq,rs}(\omega)$. Generally, the approximation schemes described for one-particle GF may also be applied to the polarization propagator. Therefore, we will not discuss it here and the reader is referred to the original articles.^{9,37} Recently, Dreuw and coworkers³⁸ have extended the ADC(2) scheme for polarization propagator to an unrestricted formulation, allowing calculation of excited states of medium-sized radicals. The results obtained by applying this method to several radical cations as well as comparison of the results to those obtained with EOM-CCSD method can be found in the work of Dreuw and coworkers.³⁸

The essential numerical tasks associated with the computation of the GF in the ADC(n) schemes involve the evaluation of matrix elements and the diagonalization of matrices defined in the space of a special class of ionic configuration. In realistic applications, the main problem is that one has to cope with the size of the configurational space. Depending on the size of the molecule, the basis set, and the approximation scheme used, the configuration space can become extremely large preventing the use of this method for large molecules. In 1998, Ortiz³⁹ suggested a simplified version of ADC(3) method. This method presents a nondiagonal, renormalized extension of the P3 quasiparticle approximation.³⁹ The terms that are typically unimportant for ionization

energies of closed-shell molecules were discarded. The new method is named the nondiagonal, renormalized, second-order (NR2) theory. The ADC(3) method requires o^2v^4 scaling, whereas NR2 calculations scale as o^2v^3 . The resulting smaller memory requirement facilitates NR2 calculations for systems where ADC(3) method is still not feasible.

Semiempirical OVGf Method

In early 1990, we have developed semiempirical variant of the OVGf method.⁴⁰⁻⁴³ It was shown in a series of papers⁴⁰⁻⁴⁵ that, in contrast to the *ab initio* OVGf method, wherein full perturbation correction (Eq. 5) for the self-energy part is required^{2,8} for quantitatively reliable results, in case of semiempirical implementation of the OVGf method inclusion of higher order terms (such as third-order truncation and renormalization factor A of the self-energy part) in the OVGf treatment does not affect the computed IPs. However, with the third order or full expansion of the self-energy part, the required Central Processing Unit (CPU) time is greatly increased compared with the second-order expansion. This feature of the semiempirical OVGf approach allows its usage as a routine method for IPs calculations of very large molecules. Semiempirical OVGf method is implemented in MOPAC93 program.⁴⁶

APPLICATIONS OF GF FORMALISM IN OTHER FIELDS

To enhance the interdisciplinary scope of the overview, various applications of GF formalism in other fields of science are briefly discussed in this section. The recent review of Dickhoff and Barbieri⁴⁷ describes applications of self-consistent GF method in nuclear physics. Results for both finite nuclei and nuclear matter are discussed with particular emphasis on clarifying the role of short-range correlations in determining various experimental quantities. Another application of GF methods in the angle-resolved photoemission studies in solids, in the high-temperature superconductors, in particular, is discussed in the review of Damascelli et al.⁴⁸ The authors have shown that in the discussion of photoemission on solids, the most powerful and commonly used approach is based on the GF formalism. Today, most characterization tools as well as electro-optical devices are based on our understanding of the interaction of photons and electrons with matter. The review of Onida et al.⁴⁹ discusses the two most widely used techniques for describing electronic excitations in infinite systems,

TABLE 1 | Vertical Ionization Energies of Free-Base Porphyrin (eV) Calculated Using AM1 Hamiltonian with KT and OVGf Approaches and KT, P3, and OVGf Methods with 6-311+G** Basis Set

MO	AM1 ¹		6-311+G** ²			Expt ⁵
	KT	OVGF ³	KT	P3 ⁴	OVGF ⁴	
b _{3u}	7.80	7.11	6.77	7.00 (0.85)	6.66 (0.87)	6.9
a _u	7.79	7.23	6.24	7.06 (0.85)	6.61 (0.87)	7.1-sh
b _{1g}	9.71	8.78	9.21	8.32 (0.81)	8.37 (0.82)	8.2-sh
b _{3u}	9.79	8.90	9.37	8.51 (0.82)	8.54 (0.83)	8.8-sh
b _{2g}	–	–	10.12	9.16 (0.68)	9.08 (0.70)	9.1
$\overline{\Delta}_{\text{abs}}$ ⁶	0.77	0.26	0.74	0.12	0.24	

¹From Ref 66.²From Ref 65.³Active space is a window with 57 occupied and 53 virtual MOs.⁴468 MOs were retained in the active space, 24 core occupied MOs were dropped. Associated pole strengths are presented in parentheses.⁵From Ref 67.⁶Mean absolute deviation between the calculated and the experimental values.

namely the GF approach to many-body perturbation theory calculations and the time-dependent density functional theory. The authors describe different approximations of the two approaches as well as the advantages and drawbacks of the methods.

Band structures are of fundamental interest to the solid-state physics as they reveal important properties of crystals. The review of Buth et al.⁵⁰ describes a crystal orbital formulation of the ADC scheme, which is termed as the crystal orbital ADC method (CO-ADC). The authors also devised a configuration selection procedure for CO-ADC approach, which can equally well be used in conjunction with the calculations of IPs and EAs of large molecules. Successful adaptation of the one-particle GF schemes to the band structure formalism of extended periodic systems, such as oligomers and clusters, was done in the works of Deleuze et al.^{51,52} and Cederbaum and coworkers.⁵³ The issue of size and charge consistency in the case of adapting ADC scheme to the formalism of crystalline orbitals for extended periodic systems is extensively discussed in the review⁵⁴ to which the interested reader is referred.

ILLUSTRATIVE APPLICATIONS OF GFs

In this section, we would like to present some illustrative examples of applying GF technique for IPs calculations of molecular systems with chemical and biological interest. Many more examples may be found in the works of Deleuze et al.^{55,56} and Ortiz and coworkers^{57–59} for relatively big molecules, as well as in the works of Trofimov and coworkers.^{60,61} for

small and medium-sized organic molecules. Recent examples of using GF calculations of one-electron and shake-up ionization energies as well as Dyson orbital electron momentum distributions for interpretation of the results of electron momentum spectroscopy may be found in the works of Deleuze and coworkers.^{62–64} Examples of using semiempirical implementation of GF can be found in the works of Danovich et al.^{40–45}

Large aromatic systems, such as porphyrins, are of substantial interest due to their great importance in a number of biochemical and chemical processes. As the first example of the applicability of the GF approach for calculating IPs of relatively big molecules of biochemical interest, we present in Table 1 results of IPs calculations of a free-base porphyrin (Figure 1, compound 1). The IPs were calculated by P3 and OVGf methods with 6-311+G** basis set using Gaussian03⁶⁵ and OVGf approach with AM1 semiempirical Hamiltonian using MOPAC93 programs.⁶⁶

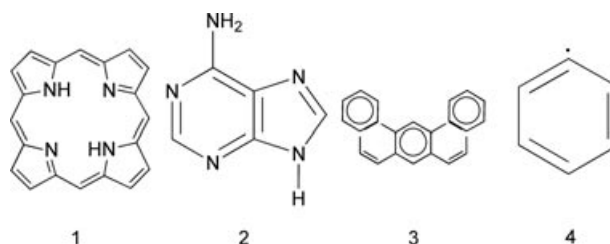
**FIGURE 1** | Structures of porphyrin (1), adenine (2), 1,2,7,8-dibenzanthracene (3) molecules, and phenyl radical (4).

TABLE 2 | Vertical Ionization Energies of Adenine Molecule (eV) Calculated Using P3, OVGf, and ADC(3) Methods with Different Basis Sets

MO	OVGF ¹		P3 ¹		ADC(3) ¹	Expt ¹
	6–31G	6–311G**	6–31G	6–311G**	6–31G	
25a	7.87	8.13	8.12	8.38	7.93	8.47
24a	9.15	9.18	9.37	9.50	9.36	9.54
23a	8.85	9.22	8.92	9.35	9.30	9.45
22a	10.12	10.3	10.15	10.44	10.26	10.51
21a	9.93	10.3	9.96	10.39	10.23	10.45
20a	10.94	11.39	10.91	11.40	11.20	11.35
19a	12.05	12.08	12.06	12.16	12.09	12.09
18a	13.42	13.43	13.37	13.46	13.54	13.20
$\overline{\Delta}_{\text{abs}}^2$	0.35	0.20	0.28	0.09	0.22	

¹From Ref 68.²Mean absolute deviation between the calculated and the experimental values.

The KT produces very bad agreement with the experimental PE spectrum. Both P3 and OVGf methods considerably improve the KT results. P3 calculations provide excellent agreement with experimental data⁶⁷ with a mean deviation of only 0.12 eV. High-pole strength values of ~ 0.85 indicate the qualitative validity of the Koopman's description of the first states of the porphyrin molecule (except for the b_{2g} state wherein the assumptions of both P3 and OVGf methods, especially regarding the diagonal self-energy approximation, may not be valid). OVGf IP values deviate from the experimental data more than those obtained with P3, especially for the b_{3u} and a_u states. The mean deviation of OVGf results is two times higher than for P3 results. It is noted that OVGf approach improves considerably the results of semiempirical AM1 calculations based on KT. The mean deviation for the first four IPs is only 0.26 eV at the OVGf level, which is around four times better than AM1 KT-based calculations and is comparable with the results of OVGf calculations with 6–311+G** basis set.

Unfortunately, it is still too difficult to apply the ADC(3) method with sufficient basis set to relatively big molecules. Table 2 presents result of P3, OVGf, and ADC(3) calculations for adenine molecule (Figure 1, compound 2) together with the experimental data recently published by Trofimov et al.⁶⁸

The complete PE spectrum (inner and outer valence) of adenine molecule was investigated. Depending on the basis sets chosen, the mean deviation between OVGf and P3 ionization energies is 0.1–0.2 eV, with a maximum difference of 0.4–0.5 eV. The P3 ionization energies agree better than the OVGf

results with the experimental values. In general, it is possible to conclude that the OVGf and P3 results are of similar quality. Except for the first two IPs, the ADC(3) values obtained using the 6–31G basis set are in even better agreement with experiment than both OVGf and P3 results. The results in both OVGf and P3 treatments improve in going from the 6–31G to the 6–311G** basis set. A similar trend in the lowest IPs has been observed by Deleuze et al.^{22,55,56} in polycyclic aromatic hydrocarbons.

Polycyclic aromatic hydrocarbons are of fundamental importance in many research fields such as astrophysics, spectroscopy, material, and life science. As the third example, we present in Table 3 the results of the ADC(3) and OVGf calculations of 1,2,7,8 isomer of dibenzanthracene (Figure 1, compound 3), recently published by Deleuze²⁴ employing various basis sets.

As ADC(3) calculations are computationally prohibitive, only 6–31G basis set was employed for 1,2,7,8 dibenzanthracene. The first scope of these types of calculations is to provide a qualitatively reliable description of the spreading of the ionization intensity over shake-up bands and to correctly identify those levels for which the orbital picture of ionization prevails. For more quantitative insights into ionization energies, the OVGf calculations using 6–31G, cc-pVDZ, and cc-pVTZ basis sets have been performed.²⁴ An examination of Table 3 demonstrates that outermost one-electron ionization energies are extremely sensitive to the size of the employed basis set, which must be at least of triple ζ quality at the OVGf level of theory.²⁴ The results presented in Table 3 also confirm the empirical rule

TABLE 3 | Vertical Ionization Energies of 1,2,7,8 Dibenanthracene Molecule (in C_{2v} Point Group Symmetry) Calculated Using OVGf and ADC(3) Methods with Different Basis Sets

MO	OVGF ¹				Expt ²
	6-31G	cc-pVDZ	cc-pVTZ	ADC(3)/6-31G ¹	
6b ₁ (π)	6.69(0.885)	7.11(0.877)	7.29(0.873)	6.81(0.856)	7.40
5a ₂ (π)	7.00(0.886)	7.40(0.878)	7.58(0.874)	7.12(0.854)	7.79
4a ₂ (π)	8.06(0.882)	8.35(0.875)	8.45(0.872)	8.18(0.848)	8.63
5b ₁ (π)	8.09(0.878)	8.40(0.871)	8.50(0.868)	8.18(0.834)	8.63 ²
4b ₁ (π)	9.16(0.867)	8.43(0.859)	9.53(0.855)	9.22(0.716)	9.53
				9.41(0.110)	
3a ₂ (π)	9.27(0.873)	9.53(0.865)	9.62(0.862)	9.36(0.806)	9.60
				9.85(0.032)	
3b ₁ (π) ³	10.22(0.856)	10.45(0.849)	10.55(0.843)	10.21(0.706)	10.34
				10.57(0.044)	
				11.90(0.020)	
				12.08(0.030)	
2a ₂ (π) ³	10.62(0.843)	10.89(0.831)	10.98(0.827)	10.62(0.599)	~10.9 ²
				10.19(0.081)	
				10.80(0.040)	
				11.08(0.020)	
33a ₁ (σ)	10.53(0.896)	10.82(0.886)	10.98(0.881)	10.77(0.890)	~10.9 ²
29b ₂ (σ)	10.71(0.895)	11.00(0.884)	11.15(0.880)	10.96(0.890)	~10.9 ²
28b ₂ (σ)	11.15(0.891)	11.42(0.880)	11.56(0.876)	11.40(0.882)	~11.2 ²
32a ₁ (σ)	11.45(0.892)	11.72(0.881)	11.86(0.876)	11.66(0.881)	~11.6 ²
2b ₁ (π) ³	11.49(0.810)	11.72(0.797)	11.81(0.790)	11.72(0.359)	~11.6 ²
				11.11(0.100)	

¹From Ref 24. Associated pole strengths are presented in parentheses.

²Assignment according to Ref 24.

³Breakdown of the orbital picture of ionization [shake-up lines in ADC(3)/6-31G calculations].

that OVGf pole strengths smaller than ~ 0.85 foretell a breakdown of the orbital picture of ionization at the ADC(3) level of theory.^{22,55,56}

The last example presents vertical excitation energy of phenyl radical (Figure 1, compound 4) recently reported by Dreuw and coworkers.³⁸ Results at the UADC(2)-x, the EOM-CCSD levels of theory and experimental data are summarized in Table 4.

In principle, the ADC(2) method is available in strict ADC(2)-s and extended ADC(2)-x variants.⁶⁹ In the latter case, doubly excited states are treated in the first-order perturbation theory, which results in a substantially better description of excited states with large double-excited character. The neutral phenyl radical exhibits C_{2v} symmetry and its ground electronic state is 2A_1 . The description of the excited states is very satisfying with the UADC(2)-x method wherein the mean deviation of the calculated excited states from experimental data is only 0.26 eV in contrast to 1.29 eV at the EOM-CCSD level. As was pointed in the original work of Dreuw and coworkers,³⁸ the generally large difference between

TABLE 4 | Comparison of the Computed Vertical Excitation Energies (eV) of the Phenyl Radical at UADC(2)-x and EOM-CCSD Levels with Experimental Data¹

Symmetry	UADC(2)-x ²	EOM-CCSD ²	Expt ²
1 ² B ₂	2.89	3.74	2.34
1 ² A ₂	3.07	4.24	
2 ² A ₁	3.74	5.37	3.13
3 ² A ₁	4.08	4.49	
1 ² B ₁	4.11	5.25	4.20
2 ² B ₁	4.31	5.67	4.32
2 ² A ₂	4.70	5.65	
2 ² B ₂	4.96	5.82	4.75
4 ² A ₁	5.45	7.87	

¹The symmetry of the electronic ground state is 2A_1 .

²From Ref 38 (6-31G* basis set was used).

the UADC(2)-x and EOM-CCSD values (amounting to about 0.9–1.1 eV) is most likely due to significant contribution of doubly excited configurations in

the description of the excited state wave functions of phenyl radical. As a result, EOM-CCSD in contrast to ADC(2)-x tends to overestimate the excitation energies of such states.

CONCLUSION

In this overview, we have shown that the computational methods derived from the one- and two-particle GF theory have been firmly established in the field

of quantum chemistry as standard tools for the calculation of various important properties of molecular systems with chemical and biological interest. One-particle GF methods provide a very convenient way for calculating ionization and electron attachment spectra. Two-particle GF method implemented in ADC approximations may be considered as an alternative to coupled cluster methods for the calculation of excitation energies. We believe, therefore, that these methods will become routine tools for the chemical community.

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