Electron Propagator Studies of Molecular Anions

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Abstract

Electron propagator (EP) or Green's function (GF) methods have been successfully employed to compute electron affinities for a large number of molecules having either a closed-shell or single-valence-hole dominant electronic configuration. The accuracy of such calculations, if carried out through third order, has often been comparable to that of reasonable configuration interaction (CI) calculations. However, as a computational tool, EP methods have not yet been adequately developed in relation to general open-shell molecules and atoms, and only recently have they begun to be generalized to describe states having two or more dominant configurations. Thus although GFs look promising as methods for *ab initio* calculation, much formal and programming work remains to be done before this approach can be said to compete with CI methods. On the other hand, GFs provide us with a mechanism for focusing on the one-electron (EP) or two-electron [polarization propagator (PP)] features of any problem. It is this fact that makes GFs an attractive route for developing chemical models which may or may not make use of experimental data. Although such a viewpoint has been widely used in solid-state physics, not enough work has been done on making models based upon the EP or PP. In this article, both the computational and formal history of GFs, as they apply particularly to molecular anion studies, are overviewed. The author's opinions concerning the current status and future development of the area constitute a large part of the presentation.

1. Introduction

Quantum-chemical studies of negative ions present special challenges [1]. Typical electron affinities (EAs) range from 0.1 to 2 eV, whereas valence and core ionization energies of neutral molecules span 5–20 eV and 100–1000 eV, respectively. To be of practical utility for studying EAs, quantum-chemical methods must have accuracies in the ±0.2 eV range.

As a result of their weak electron binding energies, the charge densities of anions are more diffuse than those of corresponding neutral species. This makes it essential that one augment conventional atomic orbital basis sets [2] with more diffuse funtions when attempting to study anions.

Before examining how electron propagator (EP) methods [3] have been utilized to probe EAs, it is appropriate to ask what the EP can be used for. First, it can be used to *compute* (within the Born–Oppenheimer approximation) EAs or electron detachment energies (DE). Within this utilization, it is important to address how accurate such computed energies are and what factors influence this accuracy.

The EP also provides an *ab initio* one-electron effective potential (the nonlocal energy-dependent self-energy) which governs the electron–molecule interaction.

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TABLE I. Comparison of EP and other EAs.*

Anion	Calculated E.A. (ev)	Experimental or Other Calculated E.A.
OH^-	1.76	1.82[a]
BeH^-	0.77	0.74[b]
CN^-	3.70	3.82[c]
Cl_2^-	2.25[h']	2.47[i]
BO^-	2.79	2.4 - 3.1[d]
HCC^-	3.18	2.942[j]
Li_2^-	0.46	
$LiNa^-$	0.45	
Na_2^-	0.42	
LiH^-	0.30	0.32[g]
	0.20	
LiF^-	0.46	
	0.42	
NaH^-	0.36	–
	0.29	
BeO^-	1.76	
	1.41	
NH_2^-	0.42	0.74[e]
NO_2^-	2.60	2.8[f]
Be_2^-	0.38	
Be_3^-	1.0	
Be_4^-	1.0	
Mg_4^-	0.49	

* All results were obtained in the author's lab except those for Cl_2^-.

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Given such an effective potential, one wonders whether it can be developed along semiempirical lines within an atomic or localized orbital representation and whether the elements of the self-energy matrix are transferable within such a basis. It may also be productive to look into performing a moment decomposition of the self-energy based upon expansions in powers of $(r_</r_>)$ with $r_>$ being identified as the radial coordinate of the "extra" electron. In this manner, one could obtain an expression for the potential energy of interaction of an electron

and the neutral target molecule in powers of r^{-1}, thereby giving the charge-dipole, charge-induced dipole, etc., contributions. Finally, in situations where core electrons produce severe difficulties for state-function-based methods the EP may show greater computational and/or formal promise.

With these ideas in mind, let us examine both the performance record of EP methods as applied to anions as well as the difficulties in improving upon existing EP methods.

2. Overview of Computational Results

How well has the EP done on atomic and molecular anions? In Table I we present several results obtained via the EP methods which are outlined briefly in Sec. 3. The precision levels of these results are very much in agreement with what Cederbaum and co-workers [4(a)], Öhrn et al. [4(b)], and Freed et al. [4(c)] have found within EP calculations of ionization potentials of neutral molecules. The following conclusions seem to have evolved from such studies:

(1) Double zeta plus polarization plus *diffuse* (for anions) basis functions are needed.

(2) A second-order treatment of the self-energy (see below) is not adequate because an accuracy of ±1 eV is unacceptable for EAs.

(3) The third-order self-energy is often adequate (±0.25 eV), although some work indicates the need to go to higher order in selected "terms" or "diagrams" (e.g., to sum orbital relaxation effects to all orders).

As a result, it appears that EP methods can, in certain circumstances, be competitive with configuration interaction (CI) methods and can yield results to within ±0.2 eV.

However, the forecast is not all good. It should have been noted that *none* of the above examples had an open-shell reference state! Either the anion or its neutral parent was closed shell. In fact, using presently available EP technology, it would be difficult to study the oxygen atom or the methylene molecule, the first being an open-shell species and the latter requiring a two-configuration reference function for its singlet state.

To understand why open-shell and multiconfigurational states present problems, let us briefly sketch what goes into formulating [3] a workable EP method and where existing methods fail.

3. Formulating EP Methods

Let us begin by considering the ingredients of any EP. The matrix representative $G(E)$ of the EP is commonly written [3,5] as follows:

$$G_{ij}(E) = (i^+|(E\hat{1} - \hat{H})^{-1}|j^+)$$
$$= \langle \psi i(E\hat{1} - \hat{H})^{-1}j^+|\psi \rangle + \langle \psi ((E\hat{1} - \hat{H})^{-1}j^+)i|\psi \rangle,$$

where ψ is the so-called reference function, $\hat{H}$ and $\hat{1}$ are the Hamiltonian and identity superoperator, and j^+ and i are the fermion electron creation and an-

nihilation operators. In order to develop any workable EP theory one needs to approximate ψ and $(E\hat{1} - \hat{H})^{-1}$ in some manner which is "balanced." Let us begin by examining possible choices for the reference function ψ.

(1) Single-determinant restricted Hartree-Fock (RHF) reference functions have been used for closed-shell systems [4(b),5–7]. This choice can yield, with a proper treatment of $(E\hat{1}-\hat{H})^{-1}$, the self-energy through *second order* in the fluctuation potential.

(2) Single-determinant unrestricted Hartree–Fock (UHF) functions or a Roothaan RHF function has been used for open-shell species [4(a),4(b),8–10]. This can also give a *second-order* self-energy.

(3) A second-order Rayleigh–Schrödinger perturbation theory (RSPT) development of the reference wavefunction (either RHF or UFH based) is capable of yielding [4(b),11] the self-energy through third order, and gives results equivalent to Cederbaum's diagrammatic approach [4(a)]. This approach has proven to be most useful but runs into difficulties when the perturbative assumption breaks down (e.g., for H_2 at large internuclear distances or for slightly stretched N_2 or for singlet CH_2).

(4) Recently, attempts have been made to incorporate more general MCSCF or CI reference states [12,13]. By moving away from the RSPT philosophy, one loses the concept of order. Hence some new criteria have to be used to "balance" the quality of the reference function with that of $(E\hat{1} - \hat{H})^{-1}$. Such MCSCF functions do not permit one to easily generate a zeroth-order one-electron Hamiltonian in terms of which the orthonormal molecular orbitals may be defined. Moreover, the use of such MCSCF reference functions in the EP gives rise to three-electron and higher density matrices, whose computational evaluation presents formidable problems.

Thus although advances are being attempted, we are not yet at the stage where very flexible MC reference functions can be employed in EP theory. As indicated above, any EP method also must involve a means for treating the superoperator resolvent. Approximations to $(E\hat{1} - \hat{H})^{-1}$ are usually based on the concept of the inner projection [14]:

$$(E\hat{1} - \hat{H})^{-1} \cong |\mathbf{h})(\mathbf{h}|E\hat{1} - \hat{H}|\mathbf{h})^{-1}(\mathbf{h}|,$$

and making some choice for the operator manifold

$$\mathbf{h} = (i^+, j^+ l^+ k, \ldots)$$

$$= (\mathbf{h}_1, \mathbf{h}_3, \ldots).$$

Also the matrix representative

$$(\mathbf{h}|E\hat{1} - \hat{H}|\mathbf{h})^{-1}$$

is usually further approximated [3] by decomposing it in to blocks arising from the $\mathbf{h}_1$, $\mathbf{h}_3$, etc., components of $\mathbf{h}$. In coming up with reasonable choices for the $\mathbf{h}$ operator manifold several things have to be kept in mind.

TABLE II. Effects of various **h** operators on ψ.

h	h ψ	CI Interpretation
$1b_1^+$	$1a_1^2 1b_1$	Dominant Anion Configuration
$2b_1^+$	$1a_1^2 2b_1 + X1b_1^2 2b_1$	Relaxation of $1b_1$ Plus Contamination
$1b_1^+ 2a_1^+ 1a_1$	$1a_1 1b_1 2a_1$	Relaxation of $1a_1$
* $2b_1^+ 1b_1^+ 1b_1$	$X 1b_1^2 2b_1$	Contamination
$2b_1^+ 1b_1^+ 1b_1^+ 1a_1 1a_1$	$X 1b_1 2a_1^2$	a_1 Pair Correlation
$2a_1^+ 2a_1^+ 1b_1^+ 1a_1 1a_1$	$1b_1 2a_1^2$	a_1 Pair Correlation

* Not allowed in **h** space according to Manne [15(a)] and Dalgaard [15(b)].

First, each **h** operator must be symmetry adapted (space and spin) so that **h** ψ has the desired symmetry given that ψ has some specified symmetry. This step is nontrivial in the case that ψ does not belong to a totally symmetrical (or degenerate) spacial representation or if ψ is a spin eigenfunction having $S \neq 0$. Secondly, the manifold **h** must be potentially complete but not over complete. Manne [15(a)] and Dalgaard [15(b)] have shown that the set $(p^+, p^+ q^+ \alpha, \ldots, \alpha^+, \alpha^+ \beta^+ p, \ldots)$ is complete when one defines particle (p,q,r) and hole (α, β, γ) with respect to any *one* configuration in the reference function. This sounds useful, but let us consider an example to see the problem that remains.

In Table II we list selected elements of the operator manifold **h** together with their effect on either of the two configuration reference functions appropriate to the $^1A_1$ state of CH_2. Only the two "active" valence orbitals of CH_2, are explicitly treated, and only those **h** operators which can generate a $^2B_1$ anion when acting on this ψ are considered. If

$$\psi = [1a_1^2 + X1b_1^2]N^{-1/2} \quad (^1A_1 \; CH_2),$$

then for a $^2B_1$ anion:

$$\mathbf{h} = 1b_1^+, 2b_1^+, 1b_1^+ 2a_1^+ 1a_1, \ldots.$$

Let us now look at the terms generated by **h** acting on ψ.

The data presented in Table II clearly illustrate that important configurations arise from the $\mathbf{h}_3$ and $\mathbf{h}_5$ spaces which, in conventional EP developments, are not treated as accurately as contributions arising from $\mathbf{h}_1$. This makes the usual

$(\mathbf{h}_1, \mathbf{h}_3, \mathbf{h}_5)$ partitioning and subsequent approximation of $(E\hat{1} - \hat{H})^{-1}$ difficult to carry through. Clearly, what is needed is a systematic operator manifold selection procedure analogous to the automated configuration selection processes [16] used by CI and MCSCF practitioners.

Thus although EP methods are presently competitive when the perturbative approach is valid, we need to generalize the development to admit general MC reference functions and "balanced" operator manifold choices.

4. Other Uses of the EP

In addition to the above role as a tool in computational quantum chemistry, there are other uses that can be made of EPs. The EP provides a reduced one-particle picture which can be a more convenient starting point for developing semiempirical approximations (parameterizations, ZDO, etc.) or examining transferability. This requires the EP to be expressed in an atomic or localized valence orbital basis [3,17]. The development of EP theory along such lines is probably essential if these methods and ideas are going to become an integral part of the chemist's vocabulary.

When studying anions (with their diffuse charge density), and especially when examining temporary (resonance continuum state) anions, it may be useful to analyze the self-energy's dependence on the radial position (r) of the "extra" electron. (Csanak and Taylor [18] used the bipolar expansion of r_{12}^{-1} to decompose the two-electron integrals appearing in the second-order self-energy. By then assuming that $r_>$ can be associated with the "extra" electron, one can obtain a "moment expansion" for the self-energy in powers of $r_>^{-1}$. The coefficients in this power series involve various moments of $r_<$. This approach should be a useful means of developing expressions for the large-r behavior of the self-energy and for thereby relating the self-energy to charge-dipole, charge-induced dipole, etc., contributions.

When studying electron–atom or electron–molecule collision resonances (shape or Feshbach), it has become fashionable to make use of complex coordinate methods [19] (CCM). In applying CCM to such problems within a wave function approach, one encounters difficulty because of the low-energy core electrons. The problem arises because it is difficult to describe a complex scaled core orbital $\phi_c(\bar{r}e^{i\beta})$ which has radial components of the form $\exp[-\alpha\, r \exp(i\beta)]$ in terms of the usual unscaled atomic orbital basis $\{\phi_i(\mathbf{r})\}$. As a result, spurious variation in the complex coordinate rotated energy expectation value (caused by this basis set inadequacy) overshadows the energy variations due to the "extra" scattering electron, thereby rendering the CCM method practically useless. In contrast, EP methods allow one to focus on a valence-level problem and thereby remove explicit considerations of the rotated core. The EP achieves this because it provides a one-electron effective potential (self-energy) that can be analytically continued to complex coordinates. This approach has recently been explored [20(a)–20(c)], and shows promise as a tool for studying shape and Feshbach resonances.

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