

On the “killer condition” in the equation-of-motion method: ionization potentials from multi-reference wave functions†

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The ionization operator Ω in the equation-of-motion (EOM) method is written in a form that satisfies the “killer condition” $\Omega^\dagger|\Psi_0\rangle = 0$ for arbitrary multiconfigurational reference states. The resulting equation for ionization potentials is equivalent to traditional EOM equation only if the reference state is an exact eigenfunction of the Hamiltonian. The new equation is insensitive to specifying either a simple metric or the “commutator metric”, and it represents a Hermitian formulation even for partially optimized wave functions. It is, however, equivalent to a multi-reference CI equation for the ionized state using the extended Koopmans ansatz.

I. Introduction

A. Ionization potentials

Ionization potentials (IPs), defined theoretically as the difference between the total energies of two species with different numbers of electrons (*e.g.* an ion and a neutral molecule), can be computed by several methods each of which belong to one of the following categories. The so-called Δ -techniques, Δ -SCF^{1,2} for example, constitute the first type of methods where separate calculations are conducted for the ion and the molecule, and the IP is obtained as the energy difference following the above definition. The second category consists of the so-called direct methods that make use of information only on the molecule, and describe ionization as a transition process. Perturbation theoretical and Green’s function methods^{3–7} fall into this category. These can be founded by the equation-of-motion (EOM) formalism that serves as a unifying tool for various approaches of the second type. Some details of this scheme will be summarized in the following subsection.

Direct methods have the ultimate advantage of being able to yield an IP in one step, not as a difference of two large numbers. These methods can also provide information on the transition process, transition probabilities for example. In addition, direct methods provide full characterization of the ionized (excited) states even when Δ methods are impractical, *e.g.*, because of convergence difficulties. In this paper, we shall consider merely direct methods, and use the EOM formalism to get equations for the IPs. We write the EOM equations in a form that always satisfies the so-called vacuum (or killer) condition for any wave function. Writing down the resulting equations, we point out that these correspond to general multi-reference CI equations determining the IPs. Although the resulting equations may be quite demanding computationally, they can be used, in principle, for arbitrary reference states. This is a great advantage over several traditional EOM-based methods that, as known⁸ and will also be illustrated here, yield meaningful IPs only if the one electron orbital set is fully optimized. Another problem of EOM-based methods is that they result in different working equations if

using a “simple” or “commutator metric” (*vide infra*)—this difficulty is also eliminated. Sample calculations for APSG (antisymmetrized product of strongly orthogonal geminals) and CISD (configuration interaction with singles and doubles) reference states illustrate the method.

Treating ionization as a transition process, that is treating ionization and excitation on an equal footing, is possible by the second quantized formalism. This is because the second quantized Hamiltonian is independent of the number of electrons, thus the molecule and its ions are different eigenstates of the same Hamiltonian. We note, however, that this is not merely a formal aspect: practical methods for computing IPs can be developed by exciting the ionized electrons onto virtual plane waves that describe unbound states.⁹

The organization of the paper is as follows. First, as part of the Introduction, we summarize some standard notions of the EOM method and the superoperator formalism. Then, in the theoretical section, we discuss the derivation of the equations for IPs in various forms, the role of the killer condition, and an equation that will be referred as MR-CI equation for IPs, satisfying the killer condition for arbitrary reference wave functions, including multi-reference states. Finally, the last section reports a few preliminary numerical examples.

B. Basic EOM scheme

EOM methods are often applied to obtain equations for excitation or ionization energies of many-electron systems.^{5,10,11} The name of this technique comes from writing the excited wave function for the n -th state as

$$|\Psi_n\rangle = \Omega|\Psi_0\rangle \quad (1)$$

where Ψ_0 is the ground state wave function, and $\Omega = |\Psi_n\rangle\langle\Psi_0|$ is a formal excitation operator. Obviously, operator Ω depends on the state index n , but we shall omit this label to simplify the notation. Making use of the Schrödinger equation $H\Psi_n = E_n\Psi_n$, upon substituting Ω into the commutator, one gets

$$[H, \Omega] = \omega\Omega \quad (2)$$

with $\omega = E_n - E_0$ being the excitation energy. Clearly, eqn. (2), which is an equation for the unknown Ω , is an analogue of Heisenberg’s equation of motion. Depending on the nature of

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the ‘‘excitation’’ operator Ω , the EOM of eqn. (2) describes excitation, electron attachment, or ionization processes, ω being the excitation, attachment or ionization energy, respectively. The latter case will be treated in this paper.

C. Superoperator formalism

It is common to write eqn. (2) in the suggestive form¹²

$$\mathcal{H}\Omega = \omega\Omega \quad (3)$$

where \mathcal{H} is the super Hamiltonian or Liouvillean that acts over the linear space of operators, its action being defined as forming the commutator of the Hamiltonian and the operator on which it is acting. The corresponding superoperator formalism^{13,14} is not merely a formalization tool, but it serves as a useful technique to specify the transition process in the general EOM scheme, as it is widely applied, *e.g.*, in the Green’s function theory.^{4,14}

The general formalism, which may in principle cover many actual approximative methods, can be developed as follows. First, we apply Löwdin’s partitioning technique¹⁵ in the operator space by introducing two orthogonal projectors \mathcal{O} and \mathcal{P} so that

$$\mathcal{I} = \mathcal{O} + \mathcal{P}, \quad (4)$$

and write the \mathcal{O} -component of the EOM as

$$\{\mathcal{O}\mathcal{H}\mathcal{O} - \mathcal{O}\mathcal{H}(\mathcal{P}\mathcal{H} - \omega)^{-1}\mathcal{P}\mathcal{H}\mathcal{O}\}\Omega = \omega\mathcal{O}\Omega \quad (5)$$

One family of methods, to which the present formulation also belongs, entirely neglects the \mathcal{P} components, and instead of eqn. (5) writes:

$$\mathcal{O}\mathcal{H}\mathcal{O}\Omega = \omega\mathcal{O}\Omega. \quad (6)$$

This is justified only if the \mathcal{O} -space provides a satisfactory description of the process. Techniques that account for the \mathcal{P} -component of the equation in different approximative manners have been developed by using either the EOM or the Green’s function approach.^{16,17} The key to the latter methods is the well-known Dyson equation,¹⁸ an analogue of eqn. (5), that gives a perturbative expansion of the resolvent of \mathcal{H} . Approximate solutions of the Dyson equation for IPs have become known by the names 2ph-TDA (two-particle-one-hole Tamm–Dankoff approximation),^{19,20} P3,²¹ SBC (shifted Born collision)²² and several others.^{12,23}

Our next step is to introduce an operator basis: $\{\Omega_i^0\}$ in which the exact excitation/ionization operator is to be expanded. If operators Ω_i^0 are formed by fermion operators of type $\{a_\mu\}$, $\{a_\mu a_\nu a_\lambda^\dagger\}$, ..., then the process to be described is an ionization, while electron attachment is specified by selecting $\{a_\mu^\dagger\}$, $\{a_\mu^\dagger a_\nu^\dagger a_\lambda\}$, Similarly, an electronic excitation is described by $\{a_\mu^\dagger a_\nu\}$, $\{a_\mu^\dagger a_\nu^\dagger a_\lambda a_\sigma\}$, Here we shall choose the first case, focusing on the ionization process. The \mathcal{O} -space is formed by a subset of the above set of operators in each case.

To proceed further, one has to introduce a metric in the operator space. The simplest choice is to define a binary product between operators as

$$\mathcal{S}_{ik} = (\Omega_i^0 | \Omega_k^0) = \langle \Psi_0 | \Omega_i^{0\dagger} \Omega_k^0 | \Psi_0 \rangle, \quad (7)$$

that clearly depends on the reference function Ψ_0 . Sometimes it is more convenient to choose the so-called commutator metric (actually anticommutators are used for fermions):

$$(\Omega_i^0 | \Omega_k^0) = \langle \Psi_0 | [\Omega_i^{0\dagger}, \Omega_k^0]_+ | \Phi_0 \rangle. \quad (8)$$

The two choices are by no means equivalent, as we shall see later.

Having defined the binary product, the resolution of projector \mathcal{O} may be given as

$$\mathcal{O} = \sum_{ik} |\Omega_i^0\rangle (\mathcal{S}^{-1})_{ik} \langle \Omega_k^0| \quad (9)$$

where the inverse metric matrix appears if the operator basis is not orthogonal. Summations over i and k run over the specified subset, and the inverse of \mathcal{S} is taken also within this subset. Substituting this projector into the \mathcal{O} -component of the EOM, and expanding the unknown ionization operator in terms of the operator basis

$$\Omega = \sum_i c_i \Omega_i^0, \quad (10)$$

we get, after straightforward algebra:

$$\sum_i (\Omega_j^0 | \mathcal{H} \Omega_i^0) c_i = \omega \sum_i \mathcal{S}_{ji} c_i \quad (11)$$

which has the form of a generalized eigenvalue problem. Solution of this equation is simple once the elements of the Hamiltonian \mathcal{H} and metric \mathcal{S} matrices are evaluated. These matrix elements depend on our choice for the operator basis Ω_i^0 and for the reference function Ψ_0 . Both questions are connected to the problem of the ‘‘killer condition’’ that will be discussed in the forthcoming section.

II. Theory

In this section, we outline an EOM-based method for computing IPs directly, and compare it to earlier schemes. These schemes may deviate from each other in the specification of the ionization operator Ω , and by selecting different metrics in the operator space.

A. Traditional EOM formulation for IPs

The simplest choice for the ionization operator is

$$\Omega = \sum_\mu c_\mu a_\mu \quad (12)$$

which corresponds to the assumption that the ionized states are just linear combinations of the simple hole states of the molecule. Although, in the light of the so-called ‘‘extended Koopmans theorem’’ (EKT)^{24–26} this may hold exactly for the first ionization potential, the conditions for EKT (the exactness of the molecular reference wave function) is hardly satisfied in practice. Therefore, we should consider eqn. (12) as an approximation, which corresponds to selecting projector \mathcal{O} as

$$\mathcal{O} = \sum_{\mu\lambda} |a_\mu\rangle (\mathcal{S}^{-1})_{\mu\lambda} \langle a_\lambda| \quad (13)$$

with the metric matrix

$$\mathcal{S}_{\mu\lambda} = (a_\mu | a_\lambda). \quad (14)$$

At this point, one has two choices. For the binary product in eqn. (14), one can either use the simple metric of eqn. (7), or the commutator metric of eqn. (8). In the latter case, the metric will be orthonormal by virtue of the Fermion anti-commutation rules:

$$\mathcal{S}_{\mu\lambda} = \langle \Psi_0 | [a_\mu^\dagger, a_\lambda]_+ | \Psi_0 \rangle = \delta_{\mu\lambda} \quad (15)$$

for any normalized Ψ_0 , while in the former case we find

$$\mathcal{S}_{\mu\lambda} = \langle \Psi_0 | a_\mu^\dagger a_\lambda | \Psi_0 \rangle = P_{\mu\lambda}, \quad (16)$$

with the elements of the first order density matrix P . The respective EOM eigenvalue problems become:

$$\sum_\mu \langle \Psi_0 | [a_\nu^\dagger, [H, a_\mu]]_+ | \Psi_0 \rangle c_\mu = \omega c_\nu \quad (17)$$

for the commutator metric, and

$$\sum_\mu \langle \Psi_0 | a_\nu^\dagger [H, a_\mu] | \Psi_0 \rangle c_\mu = \omega \sum_\mu P_{\nu\mu} c_\mu. \quad (18)$$

for the simple metric. These two equations are not equivalent in the general case. Eqn. (18) is often written in the short form

$$\mathbf{F}\mathbf{c} = \omega\mathbf{P}\mathbf{c} \quad (19)$$

where the elements of the generalized Fockian \mathbf{F} are defined as

$$F_{\mu\nu} = \langle \Psi_0 | a_\nu^\dagger [H, a_\mu] | \Psi_0 \rangle. \quad (20)$$

Note that matrix \mathbf{F} is not symmetric in general.

B. Variational arguments

The very same equations can also be obtained from a variational reasoning.⁸ Multiplying eqn. (3) by Ω^\dagger from the left we get

$$\Omega^\dagger \mathcal{H} \Omega = \omega \Omega^\dagger \Omega \quad (21)$$

which gives rise to the functional for the ionization potential

$$\omega = \frac{\langle \Psi_0 | \Omega^\dagger \mathcal{H} \Omega | \Psi_0 \rangle}{\langle \Psi_0 | \Omega^\dagger \Omega | \Psi_0 \rangle} \quad (22)$$

Variation of this functional with respect to the unknown expansion coefficients c_μ of eqn. (12) gives eqn. (18). Alternatively, adding the equation

$$\mathcal{H} \Omega \Omega^\dagger = \omega \Omega \Omega^\dagger \quad (23)$$

to eqn. (21), one obtains the functional

$$\omega = \frac{\langle \Psi_0 | \Omega^\dagger \mathcal{H} \Omega + \mathcal{H} \Omega \Omega^\dagger | \Psi_0 \rangle}{\langle \Psi_0 | \Omega^\dagger \Omega + \Omega \Omega^\dagger | \Psi_0 \rangle} \quad (24)$$

the variation of which yields eqn. (17). The significance of eqn. (23), *i.e.* the difference between (22) and (24), will be discussed below.

C. The “killer condition”

An important condition for excitation operators Ω results from the orthogonality between ground and excited state wave functions:

$$\Omega^\dagger | \Psi_0 \rangle = | \Psi_0 \rangle \langle \Psi_n | \Psi_0 \rangle = 0. \quad (25)$$

This equation expresses that the ground state cannot be de-excited, and it is often referred to as the *killer condition*. Although it emerges from the orthogonality constraint which is of extreme importance, many *ansätze* for Ω violate this condition. In particular, the *ansatz* of eqn. (12) does not satisfy it in the general case, since, for an arbitrary Ψ_0 ,

$$\Omega^\dagger | \Psi_0 \rangle = \sum_\mu c_\mu a_\mu^\dagger | \Psi_0 \rangle \neq 0, \quad (26)$$

Violation of eqn. (25) has several unfortunate consequences, *e.g.*, causing non-equivalence of alternative EOM functionals or the need of expensive orbital optimizations to get a Hermitian eigenvalue problem instead of eqn. (18) (orbital gradients are known to originate from the antisymmetric part of the generalized Fockian of eqn. (20)).⁸ Comparing eqn. (22) and (24), one observes that they are just the same if $\Omega^\dagger | \Psi_0 \rangle = 0$. Accordingly, one may conclude that the violation of the killer condition is responsible for the deviation of methods using “simple” or “commutator” metrics.

In the special case when Ψ_0 is a single determinant, the sum in eqn. (12) runs over merely occupied indices i , and, instead of eqn. (26), one writes

$$\Omega^\dagger | \Psi_0 \rangle = \sum_\mu^{occ} c_\mu a_\mu^\dagger | a_1^\dagger a_2^\dagger \dots a_N^\dagger \rangle = 0, \quad (27)$$

thus we see that the killer condition is satisfied in the single determinantal (*e.g.*, Hartree–Fock) limit. However, it is satisfied for a *wrong reason*: eqn. (27) vanishes due to the Pauli

principle, *i.e.*, because one cannot re-create an occupied orbital. As soon as Ψ_0 is multiconfigurational, this will no longer be a forcing factor, and the killer condition will not be satisfied automatically.

The “*good reason*” for which eqn. (25) should rather be satisfied is the orthogonality of Ψ_0 to Ψ_n . By an appropriate definition of Ω , in replacement of eqn. (12), this can be easily incorporated. If we accept the *ansatz* of eqn. (12) for Ψ_n , and substitute it into the definition of Ω , we may formally write:

$$\Omega = | \Psi_n \rangle \langle \Psi_0 | = \sum_\mu c_\mu a_\mu | \Psi_0 \rangle \langle \Psi_0 |, \quad (28)$$

the main difference from eqn. (12) being shown by the appearance of the ground state projector $| \Psi_0 \rangle \langle \Psi_0 |$. The adjoint of this excitation operator trivially satisfies the killer condition for arbitrary N -electron reference states, since

$$\Omega^\dagger | \Psi_0 \rangle = \sum_\mu c_\mu | \Psi_0 \rangle \langle \Psi_0 | a_\mu^\dagger | \Psi_0 \rangle = 0. \quad (29)$$

We interpret eqn. (28) so that the basis operators are now redefined as

$$\Omega_\mu^0 = a_\mu | \Psi_0 \rangle \langle \Psi_0 |. \quad (30)$$

It may be interesting to note that an entirely different approach that also satisfies the killer condition was proposed by Prasad *et al.*²⁷ In this paper the ground state wave function is obtained by an exponential wave operator using an anti-Hermitian cluster operator, and a unitary wave operator thereby. The vacuum condition is ensured by defining effective ionization operators that include the inverse of the unitary wave operator. The main difference between this method and the one presented here is that the former is bound to coupled-cluster type reference states with unitary exponential *ansatz*, while we do not apply any restriction on the form of the ground state wave function.

Size-consistent procedures that can also satisfy the killer condition by the choice of the operator manifold were obtained in the Fock space coupled cluster method. The primary ionization potentials and electron affinities were reported to be equivalent^{28–30} to those obtained by the EOMIP-CC or EOMEA-CC methods.^{30–33} Some numerical comparison to the latter method will be shown in section III.

D. MR-CI equations for ionization potentials

Substituting the redefined operators in the form of (30) into the EOM equation (11), one obtains, instead of (18), the following equation for the ionization potentials ω and the expansion vectors \mathbf{c} :

$$\sum_\mu (\langle \Psi_0 | a_\nu^\dagger H a_\mu | \Psi_0 \rangle - \langle \Psi_0 | H | \Psi_0 \rangle P_{\nu\mu}) c_\mu = \omega \sum_\mu P_{\nu\mu} c_\mu \quad (31)$$

Introducing the Hamiltonian matrix elements $H_{\nu\mu} = \langle \Psi_0 | a_\nu^\dagger H a_\mu | \Psi_0 \rangle$ and the ground state expectation value $E_0 = \langle \Psi_0 | H | \Psi_0 \rangle$, this can be written as

$$(\mathbf{H} - E_0 \mathbf{P})\mathbf{c} = \omega \mathbf{P}\mathbf{c} \quad (32)$$

which is a generalized Hermitian eigenvalue problem. It can be considered as a kind of internally contracted MR-CI equation for the ion written in the basis set of non-orthogonal states $a_\mu | \Psi_0 \rangle$. It is not difficult to see that the very same equation results if one uses the commutator metric (*cf.* eqn. (17)).

To compare eqns. (31) and (18), one may expand the commutator in the latter to write

$$\sum_\mu (\langle \Psi_0 | a_\nu^\dagger H a_\mu | \Psi_0 \rangle - \langle \Psi_0 | a_\nu^\dagger a_\mu H | \Psi_0 \rangle) c_\mu = \omega \sum_\mu P_{\nu\mu} c_\mu. \quad (33)$$

which is equivalent to eqn. (31) if $|\Psi_0\rangle$ is an exact eigenfunction of H .

When eqns. (31) and (18) are different, the former has to be preferred since, besides being consistent with the killer condition, it represents an inherently Hermitian formulation of the ionization problem. In contrast, eqn. (18) deals with a matrix that is not Hermitian in general, the Hermiticity of the matrix at the left-hand side being known to be the stationarity condition of the energy with respect to orbital mixing.⁸

With the choice for the ionization operator (28), the EOM equation goes over to the matrix representation of the standard Schrödinger equation, $H\Psi_n = E_n\Psi_n$ for the ion, with Ψ_n being defined by eqn. (1):

$$\sum_{\mu} H_{\nu\mu} c_{\mu} = E_n \sum_{\mu} P_{\nu\mu} c_{\mu}, \quad (34)$$

which can be brought to a form equivalent to (31) by writing $E_n = E_0 + \omega$. This gives rise to a further advantage of eqn. (31), namely, that it can be derived from the variational condition

$$\delta[\langle\Psi_n|H|\Psi_n\rangle - E_n\langle\Psi_n|\Psi_n\rangle] = 0. \quad (35)$$

The analogue of eqn. (31), where the configurations are augmented with two-hole-one-particle states, is a usual CI equation for the ion, provided that Ψ_0 is a single determinantal reference state, *e.g.*, the Hartree–Fock wave function. Such single-reference CI calculations are routinely applied to compute photoelectron spectra.³⁴ In the present formulation, however, the single determinantal nature of the reference state was not utilized, Ψ_0 being considered as the ground state wave function of the parent molecule which can even be the exact solution or any approximation thereof. Accordingly, eqn. (31) can be considered as a special multi-reference CI equation for ionization potentials, where the configurations are generated by acting with a_{μ} on the reference state Ψ_0 that is kept fixed in the spirit of the “internally contracted” scheme. The applicability of the method depends on the ease of evaluating the matrix elements of the Hamiltonian.

III. Numerical illustrations

Extensive numerical results will be published in a subsequent paper. Here we report only a few preliminary numbers computed in small basis sets to illustrate the differences between IPs obtained from eqns. (17), (18) and (32). Since the conditions for the EKT are far from being satisfied in small bases, we cannot expect good values for the IPs—that would require, at least, the inclusion of two-hole–one-particle states as well.

The working equation of the present paper, eqn. (32), does not bring any new features in two special cases: if the reference function is either a single determinant (the Hartree–Fock case) or it is exact in the given basis set (the full-CI case). In both cases the generalized Fockian is symmetric, there are no nonzero orbital gradients, the killer condition is automatically satisfied, and the two forms of the EOM (that use the simple or commutator metric) are equivalent. In between, there is a large variety of correlated wave functions that lack orbital optimization, thus they are worth investigating as reference

states in eqn. (32). Two of them, the antisymmetrized product of strongly orthogonal geminals (APSG),^{35–40} and the standard CISD state is tested below. Orbital optimization is especially important for APSG, since it is an MC-SCF type wave function, while it has a marginal importance in the case of CISD where, merely, the mixing of occupied and virtual MOs counts.

A. APSG reference state

Details of the APSG theory are described elsewhere, see, *e.g.*, ref. 40 and references therein. Here we mention only that it is a size extensive/consistent wave function that is variational, properly dissociating, and exact for two electrons. It can be considered as a special MCSCF or as a generalized GVB wave function.⁴¹ Though the orbital optimization is important for APSG, it is quite expensive to perform, and one often uses approximate orbitals instead, which can be constructed from canonical Hartree–Fock MOs by a localization procedure.

In Table 1, we present a few IPs obtained for water in a valence TZP (6-311G**) basis set, and for the nitrogen molecule in valence TZ (6-311) basis. We compare the four versions computed with the here-presented formulae obtained with the APSG reference state, standard Hartree–Fock (the Koopmans values), and the EOMIP-CCSD method that is a CCSD calculation for IPs and is considered to be quite accurate.^{30–33} One of the above mentioned four versions is the fully optimized APSG (5th column in Table 1), three others apply Boys’ localized MOs⁴² instead of the optimized orbitals. Two of these three use eqn. (32) or (18) to compute IPs, while the third one corresponds to the commutator metric (eqn. (17)). When using eqn. (18) with unoptimized wave functions, prior to solving the eigenvalue problem we have symmetrized the generalized Fockian by taking its Hermitian part.

For the first IP of water the Koopmans value is not that bad, and the result obtained with the commutator metric (eqn. (17)) is quite close to it even though no orbital optimization was performed. In turn, eqn. (18) with unoptimized orbitals produces a very bad result (0.3385 E_h). Using eqn. (32), still with unoptimized (Boys’) MOs, improves the IP significantly, the difference between the optimized and unoptimized case being reduced to 0.0148 E_h .

The example of the nitrogen molecule is even more instructive. Here we face the well known problem that the Hartree–Fock (HF) method (except for the case of minimal basis) interchanges the order of the σ and π orbitals, predicting the latter to be of lower energy. Correlated methods, in accordance with experimental results, show that the first IP is of type σ . Calculation with the commutator metric does not fix the qualitative error of HF, neither does unoptimized APSG with eqn. (18) moreover it worsens the numbers. However, upon using eqn. (32) with unoptimized orbitals, the order of the two IPs comes out correctly, and the values are also much closer to those obtained by optimized orbitals with APSG or to those of the EOMIP-CCSD method. We note that good numerical agreement cannot be expected, since in the working eqn. (32) we are dealing with the simple 1h (one-hole) ionization process, while 1p2h (one-particle–two-hole) processes are known to improve the accuracy significantly.

Table 1 Ionization potentials for water and the N_2 molecule (E_h); APSG reference state

	Koopmans	Unoptimized APSG			Optimized APSG	EOMIP-CCSD
		Eqn. (17)	Eqn. (18)	Eqn. (32)		
H_2O	0.4999	0.5067	0.3385	0.5028	0.4880	0.4422
N_2 σ	0.6299	0.6301	0.7550	0.6189	0.6057	0.5467
π	0.6221	0.6229	0.4832	0.6349	0.6541	0.6360

Table 2 First ionization potentials for the Be atom (E_n); optimized APSG reference state (the experimental value is 0.3426 E_n)

Basis set	Koopmans	Full CI	EOMIP-CCSD	Commutator metric	Simple metric
STO-3G	0.2540	0.3055	0.3054	0.2198	0.3055
4-31G	0.2920	0.3330	0.3331	0.2616	0.3331
6-311G	0.3089	0.3405	0.3406	0.2786	0.3408
6-311G**	0.3089	0.3412	0.3413	0.2794	0.3414

In Table 2, we compare the IPs of the Be atom as obtained with the optimized APSG reference state using the simple metric eqn. (18), and the commutator metric (eqn. (17)). Koopmans values, Δ -full CI IPs, and the EOMIP-CCSD results are shown for comparison. The numbers clearly indicate that the performance of the commutator metric is quite bad: in all quoted cases the Koopmans values are worsened by eqn. (17), while the first IP from eqn. (18) is quite accurate for this system.

B. CISD reference state

In the case of the APSG reference state, the usefulness of eqn. (32) as compared to eqn. (18) is not so pronounced, since the orbitals of this wave function can always be optimized variationally without much difficulty, and in that case the two equations are equivalent. The case of the CISD reference state is more interesting, since orbital optimization for this wave function is not feasible in general (though, of course, only the occupied-virtual mixing would count). Here we present a few numerical results obtained with eqns. (18) and (32) for the first IP of the Be atom, using the CISD density matrices to characterize the reference state.

Evaluation of the Hamiltonian matrix elements in eqn. (32) requires knowledge of the third order density matrix. The simple structure of the APSG wave function permits one to evaluate this matrix exactly at a low cost. For CISD, computation and storage of the third order density matrix is quite demanding. One possibility to avoid this problem would be the application of approximate formulae for higher order density matrices.^{43–46} Here, restricting ourselves to small basis sets, we applied the following procedure, which yields exact results for the Hamiltonian matrix elements. The latter can be given as

$$\langle \Psi_0 | a_v^\dagger H a_\mu | \Psi_0 \rangle = \langle \Psi_0 | a_v^\dagger a_\mu H | \Psi_0 \rangle + F_{v\mu}, \quad (36)$$

where the generalized Fock matrix elements are defined by eqn. (20), and can be computed without any difficulty. As to the first term on the right-hand side, though not cheaply, it can be evaluated by a sufficiently flexible CI program noting that the vector $|\sigma\rangle = H|\Psi_0\rangle$ is easy to construct. Then, the required term arises simply as $\langle \Psi_0 | a_v^\dagger a_\mu |\sigma\rangle$, at a price of evaluating a first order density matrix. However, since the operator string $a_v^\dagger a_\mu$ represents a single substitution, vector σ has to be computed in the subspace that includes triply excited configurations, if Ψ_0 is a CISD state. We have evaluated these quantities by a general determinant-based CI/CC program written recently in our laboratory.⁴⁷

For the CISD wave function, orbital optimization is less important than for an MC-SCF type function, therefore the differences between eqns. (19) and (32) are expected to be

Table 3 First ionization potentials for the Be atom (E_n); CISD reference state

Basis set	Koopmans	Full CI	Eqn. (19)	Eqn. (32)
3-21G	0.3056	0.3407	0.3410	0.3408
6-311G	0.3089	0.3405	0.3388	0.3397
6-311G**	0.3089	0.3412	0.3392	0.3402

minor. This is indeed shown in Table 3 where results for the first IP of the Be atom are presented, in comparison with the Koopmans and full-CI values. However, the use of eqn. (32) still improves the numbers in each case. We note that this is by no means necessary: in cases where higher excited configurations are important, the lack of two-hole–one-particle terms in the CI problem may result in quite bad IPs.

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References

- 1 P. Čarsky and M. Urban, *Ab Initio Calculations*, Springer, Heidelberg, *Lecture Notes in Chemistry*, vol. 16, 1980.
- 2 G. Born, H. A. Kurtz and Y. Öhrn, *J. Chem. Phys.*, 1977, **68**, 74.
- 3 J. Oddershede, in *Advances in Chemical Physics*, John Wiley & Sons, New York, 1987, vol. 69, p. 201.
- 4 Y. Öhrn and G. Born, *Adv. Quantum Chem.*, 1981, **13**, 1.
- 5 K. F. Freed, D. L. Yeager and M. F. Herman, *Adv. Chem. Phys.*, 1981, **48**, 1.
- 6 L. S. Cederbaum and W. Domcke, *Adv. Chem. Phys.*, 1977, **36**, 205.
- 7 B. T. Pickup and O. Goscinski, *Mol. Phys.*, 1973, **26**, 1013.
- 8 R. McWeeny, *Methods of Molecular Quantum Mechanics*, Academic, London, 1989.
- 9 J. F. Stanton and J. Gauss, *J. Chem. Phys.*, 1999, **111**, 8785.
- 10 D. F. Rowe, *Rev. Mod. Phys.*, 1968, **40**, 153.
- 11 P. R. Surján, *Croat. Chem. Acta*, 1998, **71**, 489.
- 12 G. D. Purvis and Y. Öhrn, *Int. J. Quantum Chem.*, 1977, **S11**, 359.
- 13 H. Primas, *Rev. Mod. Phys.*, 1963, **35**, 710.
- 14 B. Pickup and O. Goscinski, *Mol. Phys.*, 1973, **26**, 1013.
- 15 P. Löwdin, *J. Mol. Spectrosc.*, 1963, **10**, 12.
- 16 J. Simons and W. D. Smith, *J. Chem. Phys.*, 1973, **58**, 4899.
- 17 J. V. Ortiz, *Adv. Quantum Chem.*, 1999, **35**, 33.
- 18 F. J. Dyson, *Phys. Rev.*, 1949, **75**, 1736.
- 19 J. Schirmer and L. S. Cederbaum, *J. Phys. B*, 1977, **11**, 1889.
- 20 M. Mishra and Y. Öhrn, *Chem. Phys. Lett.*, 1980, **71**, 549.
- 21 J. V. Ortiz, *J. Chem. Phys.*, 1996, **104**, 7599.
- 22 G. D. Purvis and Y. Öhrn, *J. Chem. Phys.*, 1974, **60**, 4063.
- 23 P. Jørgensen and J. Simons, *J. Chem. Phys.*, 1975, **63**, 5302.
- 24 D. W. Smith and O. W. Day, *J. Chem. Phys.*, 1975, **62**, 113.
- 25 O. W. Day, D. W. Smith and R. C. Morrison, *J. Chem. Phys.*, 1975, **62**, 115.
- 26 J. Cioslowski, P. Piskorz and G. Liu, *J. Chem. Phys.*, 1997, **107**, 6804.
- 27 M. D. Prasad, S. Pal and D. Mukherjee, *Phys. Rev. A*, 1985, **31**, 1287.
- 28 D. Mukhopadhyay, S. Mukhopadhyay, R. Chaudhuri and D. Mukherjee, *Theor. Chim. Acta*, 1991, **80**, 441.
- 29 D. Sinha, S. K. Mukhopadhyay, R. Chaudhuri and D. Mukherjee, *Chem. Phys. Lett.*, 1989, **154**, 544.
- 30 M. Nooijen and R. J. Bartlett, *J. Chem. Phys.*, 1995, **102**, 3629.
- 31 A. Haque and D. Mukherjee, *J. Chem. Phys.*, 1984, **80**, 5058.
- 32 R. Chaudhuri, D. Mukhopadhyay and D. Mukherjee, *Chem. Phys. Lett.*, 1989, **162**, 393.
- 33 J. F. Stanton and J. Gauss, *J. Chem. Phys.*, 1994, **101**, 8938.

- 34 C. W. Murray and E. R. Davidson, *Chem. Phys. Lett.*, 1992, **190**, 231.
- 35 A. C. Hurley, J. Lennard-Jones and J. A. Pople, *Proc. R. Soc. London, Ser. A*, 1953, **220**, 446.
- 36 J. M. Parks and R. G. Parr, *J. Chem. Phys.*, 1957, **28**, 335.
- 37 E. Kapuy, *Acta Phys. Hung.*, 1959, **10**, 125.
- 38 E. Kapuy, *Chem. Phys. Lett.*, 1968, **3**, 43.
- 39 W. Kutzelnigg, *J. Chem. Phys.*, 1964, **40**, 3640.
- 40 P. Surján, *Top. Curr. Chem.*, 1999, **203**, 63.
- 41 F. W. Bobrowicz and W. A. Goddard III, in *Methods of Electronic Structure Theory*, ed. H. F. Schaefer III, Plenum, New York, 1977, p. 79.
- 42 S. F. Boys, *Rev. Mod. Phys.*, 1960, **32**, 296.
- 43 C. Valdemoro, *Phys. Rev. A*, 1992, **45**, 4462.
- 44 F. Colmenero, C. P. del Valle and C. Valdemoro, *Phys. Rev. A*, 1993, **47**, 971.
- 45 F. Colmenero and C. Valdemoro, *Phys. Rev. A*, 1993, **47**, 979.
- 46 C. Valdemoro, L. M. Tel and E. Perez-Romero, *Adv. Quantum Chem.*, 1997, **28**, 33.
- 47 M. Kállay and P. R. Surjan, *J. Chem. Phys.*, 2000, **113**, 1359.
- 48 R. A. Poirier and M. Peterson, *MUNGAUSS* Program, Department of Chemistry, Memorial University, St. Johns, Canada, 1989.