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Extended random phase approximation method for atomic excitation energies from correlated and variationally optimized second-order density matrices

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ABSTRACT

Density matrix methods are typically ground state methods. They cannot describe excited states with the same symmetry as the ground state because they rely on energy minimization. The Random Phase Approximation (RPA) is a simple method to derive excitation energies from idempotent first-order density matrices, but the quality of the resulting excitation energies is poor. The quality of the excitation spectrum may be improved by extending the RPA to correlated states. Such an 'extended RPA' (ERPA) method depends only on the second-order density matrix (2DM). This work studies the main differences between the ERPA and the RPA – the influence of electron correlation, variational optimality, the ensemble nature of the density matrix and N-representability errors in the input 2DM – by applying the ERPA to exact 2DM's and variationally optimized 2DM's. Our findings are relevant for all methods similar to ERPA that determine excitation spectra from low-order density matrices. The inclusion of correlation makes it possible to describe the low-energy excitation spectra of the atoms He–Ne adequately, and the ERPA is thus a good starting point for further refinements, as higher-order excitations should be included to obtain chemical accuracy for many-electron systems. However, the ERPA fails for ensemble density matrices and requires a positive-definite double commutator matrix $\left\langle \Psi_0 \middle| \left[a_k^\dagger a_l, \left[H, a_j^\dagger a_i\right]\right] \middle| \Psi_0 \right\rangle$ to guarantee that the excitation spectrum is real.

1. Introduction: how to compute excited states from ground-state density matrices?

Density matrix methods typically calculate ground states. Computing the density matrix for an excited state in a similar manner is not trivial, because special energy functionals or N-representability conditions are needed to distinguish the excited state from the ground state. These difficulties provide an incentive for alternative methods to extract the excitation energies directly from the ground-state density matrix.

The Equations of Motion (EOM) [1,2] relate the exact excitation energies of a chemical system to its ground state. In their exact form they are intractable, but they can be simplified in two respects: the description of correlation in the ground state can be approximated and the description of the excited states can be simplified to include only one- or two-electron excitations from the ground state. Originally, these equations have been applied to idempotent one-matrices to derive the Random Phase Approximation (RPA) [3]. They have been extended in various ways to 'Higher Random Phase Approximations' [4,5] and have even been solved self-consistently to yield ground-state density matrices in addition to excitation energies [6,7].

Approximate EOM easily connect to density matrix methods because they only require low-order ground-state density matrices as input. They have therefore been adopted in first order Density Matrix Functional Theory [8] and in second-order Density Matrix Theory [9–12]. The order of the density matrices the EOM depend on can be limited by choosing a few-electron description of the excitations. Furthermore, the dependence of the EOM on higher-order density matrices can be eliminated for instance by considering an (anti-) Hermitian subspace, as in the Hermitian Operator Method [9–12] or by approximating the higher order density matrices with an expansion in terms of lower order cumulants [12,8].

This work explores this old idea in a new context: the EOM can be used to compute excitation energies from variationally optimized second-order density matrices. In their simplest form, the

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equations include only one-electron excitations from the correlated ground state, such that they formulate a generalized eigenvalue problem in terms of the first-order density matrix (1DM) and second-order density matrix (2DM). We can thus apply this method to calculate approximate excitation energies from 2DM's obtained from the variational 2DM (v2DM) method [13–15]. This idea forms an alternative to direct variational optimization of the excited state 2DM, which would require non-trivial excited-state N-representability conditions. We shall call this method the 'Extended RPA' (ERPA) method, in accordance with the work of Pernal [8]. The ERPA method differs from similar methods previously applied to the variationally optimized 2DM's [12,13] because it does not require an approximation to the 3DM.

More specifically, this paper examines the main motivation for using ERPA over RPA – the inclusion of correlation effects – and its possible limitations due to two approximations:

- The input 2DM's in general are not exact, may represent an ensemble of states and may not be N-representable.
- The ERPA method truncates the description of the excited states by including only one-electron excitations from the correlated ground state.

Section 4 first of all demonstrates the effect of correlation, ensemble nature, and N-representability errors on the ERPA spectrum by comparing the ERPA results from uncorrelated and variationally optimized 2DM's with those from exact 2DM's; and secondly demonstrates the effect of the approximations made in the ERPA method itself by comparing the ERPA spectra to exact and experimentally determined spectra. Section 2 first presents the Equations of Motion in the present context and Section 3 comments on the details of our calculations.

2. The extended RPA method: a method to extract excitation energies from ground-state 2DM

The original framework for the Equations of Motion for the RPA was proposed by Rowe in the 1960s [2]. An exact excited state $|\Psi_n\rangle = \widehat{Q}_n^\dagger|\Psi_0\rangle$ satisfies

$$\left[\widehat{H}, \widehat{Q}_n^\dagger\right]|\Psi_0\rangle = (E_n - E_0)\widehat{Q}_n^\dagger|\Psi_0\rangle$$

Choosing the bra to be an arbitrary state $\widehat{A}^\dagger|\Psi_0\rangle$ leads to a set of equations

$$\left\langle \Psi_0 \middle| \widehat{A}\left[\widehat{H}, \widehat{Q}_n^\dagger\right] \middle| \Psi_0 \right\rangle = (E_n - E_0)\left\langle \Psi_0 \middle| \widehat{A}\widehat{Q}_n^\dagger \middle| \Psi_0 \right\rangle$$

Since $\widehat{Q}_n^\dagger = |\Psi_n\rangle\langle\Psi_0|$, its Hermitian conjugate annihilates the ground state

$$\widehat{Q}_n|\Psi_0\rangle = 0$$

so the above equations can be cast in a more symmetrical, equivalent, form

$$\left\langle \Psi_0 \middle| \left[\widehat{A}, [\hat{H}, \widehat{Q}_n^\dagger]\right] \middle| \Psi_0 \right\rangle = (E_n - E_0)\left\langle \Psi_0 \middle| \left[\widehat{A}, \widehat{Q}_n^\dagger\right] \middle| \Psi_0 \right\rangle$$

These are the Equations of Motion, which are in principle exact. However, in order to keep calculations tractable, the excitation operators $\widehat{Q}_n^\dagger$ can be approximated by one-body operators.

The usual RPA then makes an additional approximation: it evaluates the expectation values that occur in the EOM on an uncorrelated Hartree–Fock ground state Ψ_0. For such a state, the only terms in the excitation operator that lead to non-vanishing equations are hole-particle and particle-hole excitations, $\widehat{Q}_n^\dagger = \sum_{h=1}^{N}\sum_{p=N+1}^{K} X_{ph}a_p^\dagger a_h - Y_{ph}a_h^\dagger a_p$ with N the number of electrons and K the single particle basis dimension. For a correlated ground state, however, the form of the excitation operators can be generalized to include all one-electron excitations, $\widehat{Q}_n^\dagger = \sum_{ij=1}^{K} c_{ij}^n a_j^\dagger a_i$. Such a generalized excitation operator leads to the 'extended RPA' (ERPA) equations

$$\sum_{ij} c_{ij}^n \left\langle \Psi_0 \middle| \left[a_k^\dagger a_l, \left[\hat{H}, a_j^\dagger a_i\right]\right] \middle| \Psi_0 \right\rangle = (E_n - E_0)\sum_{ij} c_{ij}^n \left\langle \Psi_0 \middle| \left[a_k^\dagger a_l, a_j^\dagger a_i\right] \middle| \Psi_0 \right\rangle \tag{1}$$

For an uncorrelated Hartree–Fock ground state, these equations reduce to the usual RPA equations. For a correlated ground state, they depend on the 1DM and 2DM. Even for the exact wave function they depend only on the 1DM and 2DM, which is a consequence of the one-electron description of the excitation operator. This generalized eigenvalue problem can thus be solved to obtain approximate excitation energies $\epsilon_n = E_n - E_0$ and the corresponding expansion coefficients of the excited states, c_{ij}^n.

Like the RPA excitation energies, the ERPA excitation energies come in pairs $(\epsilon_n, -\epsilon_n)$ due to the special symmetry of the commutator matrices. The double commutator matrix on the left-hand side and the single-commutator matrix on the right hand side of Eq. (1) are symmetric

$$\begin{aligned} \left\langle \Psi_0 \middle| \left[a_k^\dagger a_l, \left[\hat{H}, a_j^\dagger a_i\right]\right] \middle| \Psi_0 \right\rangle &= \left\langle \Psi_0 \middle| \left[a_i^\dagger a_j, \left[\hat{H}, a_l^\dagger a_k\right]\right] \middle| \Psi_0 \right\rangle \\ \left\langle \Psi_0 \middle| \left[a_k^\dagger a_l, a_j^\dagger a_i\right] \middle| \Psi_0 \right\rangle &= \langle \Psi_0 | [a_i^\dagger a_j, a_l^\dagger a_k] | \Psi_0 \rangle \end{aligned} \tag{2}$$

and have the additional symmetry

$$\begin{aligned} \left\langle \Psi_0 \middle| \left[a_k^\dagger a_l, \left[\hat{H}, a_j^\dagger a_i\right]\right] \middle| \Psi_0 \right\rangle &= \left\langle \Psi_0 \middle| \left[a_l^\dagger a_k, \left[\hat{H}, a_i^\dagger a_j\right]\right] \middle| \Psi_0 \right\rangle \\ \left\langle \Psi_0 \middle| \left[a_k^\dagger a_l, a_j^\dagger a_i\right] \middle| \Psi_0 \right\rangle &= -\langle \Psi_0 | [a_l^\dagger a_k, a_i^\dagger a_j] | \Psi_0 \rangle \end{aligned} \tag{3}$$

These symmetry properties lead to pairs of eigenvalues $(\epsilon_n, -\epsilon_n)$ in the ERPA spectrum.

When the ground state Ψ_0 is the exact ground state, the double commutator matrix is also positive semi-definite: since any state of the form $\sum_{ij} c_{ij} a_j^\dagger a_i|\Psi_0\rangle$ has higher energy than the ground state

$$\sum_{ijkl} c_{kl}^* \left\langle \Psi_0 \middle| \left[a_k^\dagger a_l, \left[\hat{H}, a_j^\dagger a_i\right]\right] \middle| \Psi_0 \right\rangle c_{ij} = \sum_{ijkl} c_{kl}^* \left\langle \Psi_0 \middle| a_k^\dagger a_l (\hat{H} - E_0) a_j^\dagger a_i \middle| \Psi_0 \right\rangle c_{ij} \tag{4}$$

$$+ \sum_{ijkl} c_{kl}^* \left\langle \Psi_0 \middle| a_j^\dagger a_i (H - E_0) a_k^\dagger a_l \middle| \Psi_0 \right\rangle c_{ij}$$

$$\geqslant 0 \tag{5}$$

3. Computational details

We used GAMESS [16] to carry out the full diagonalization of the CI matrix to obtain the FCI ground state and its exact excitation energies and subsequently calculated the FCI ground-state 2DM with our own routines. We computed the variationally optimized second-order density matrices by means of a logarithmic barrier method [17]. In the variational optimization, we constrained the 2DM to have the correct normalization and to satisfy the 2-positivity conditions [17] but did not impose explicit spin conditions [18]. The approximate excitation energies for these 2DM's then follow from the generalized eigenvalue problem (1). We solved this generalized eigenvalue problem using LAPACK's dggev routine [19], which yields the generalized eigenvalues as ratio's a/b. Singularities in the metric matrix on the right hand side of Eq. (1) may give rise to eigenvalues $a/0$, but these are do not correspond to physical excitation energies.

All calculations use the Cartesian cc-pVDZ basis set as listed on the EMSL Basis Set Exchange [20,21], except for the calculations on the noble gases, which use the Cartesian aug-cc-pVTZ basis

Table 1
The ERPA excitation energies (in eV) computed from exact 2DM's for the lowest-energy excitations (as they appear in the v2DM ERPA spectrum) have relatively small errors $\Delta\epsilon_{\text{ERPA}-\text{FCI}}$ compared to the exact excitation energies ϵ_{FCI}, even for the difficult cases B–F. For these atoms, the ERPA excitation energies computed from the variationally optimized 2DM have big errors $\Delta\epsilon^{\text{v2DM}-\text{FCI}}_{\text{ERPA}}$ compared to the ERPA results from the exact 2DM.

				ϵ_{FCI}	$\epsilon_{\text{expt.}}$	$\Delta\epsilon^{\text{v2DM}-\text{FCI}}_{\text{ERPA}}$	$\Delta\epsilon_{\text{ERPA}-\text{FCI}}$	$\Delta\epsilon_{\text{RPA}-\text{FCI}}$
He	$1s^2$	$^1S \rightarrow 1s^1 2s^1$	^3S	19.833	19.820	0.000	0.001	−0.089
Li	$2s^1$	$^2S \rightarrow 2p^1$	^2P	1.841	1.848	0.005	0.002	0.003
Be	$2s^2$	$^1S \rightarrow 2s^1 2p$	^3P	2.752	2.725	0.002	0.019	Unstable
B	$2s^2 2p^1$	$^2P \rightarrow 2s^1 2p^2$	^4P	3.513	3.579	2.674	0.069	−2.335
C	$2s^2 2p^2$	$^3P \rightarrow 2\ s^1 2p^3$	^5S	3.935	4.183	7.209	0.106	−2.248
N	$2s^2 2p^3$	$^4S \rightarrow 2\ s^1 2p^4$	^4P	11.245	10.924	3.285	0.271	−0.940
O	$2s^2 2p^4$	$^3P \rightarrow 2\ s^1 2p^5$	^3P	16.204	15.655	6.872	0.950	0.016
F	$2s^2 2p^5$	$^2P \rightarrow 2\ s^1 2p^6$	^2S	22.246	21.056	11.309	1.630	0.961
Ne	$2s^2 2p^6$	$^1S \rightarrow 2\ s^2 2p^5 3p^1$	^3P	18.004	16.619	−0.047	0.474	1.345

without its D and F functions to keep the number of basis functions within an allowable range for FCI. For comparison, experimental excitation energies from the NIST atomic spectra database [22,23] are also listed. All excitation energies and energy differences are expressed in eV.

4. ERPA excitation spectra: effects of correlation, N-representability, and approximations in the method

The variational optimality of the exact ground-state 2DM and variationally optimized 2DM guarantees that the ERPA spectrum is real. In traditional RPA, instabilities in the uncorrelated ground state may lead to imaginary eigenvalues. For the exact ground state, however, the ERPA excitation energies must be real: in this case, the double commutator matrix with the elements $\left\langle \Psi_0 \middle| \left[a_k^\dagger a_l, \left[H, a_j^\dagger a_i \right] \right] \middle| \Psi_0 \right\rangle$ on the left-hand-side of Eq. (1) is symmetric positive semi-definite and the single commutator matrix with elements $\left\langle \Psi_0 \middle| \left[a_k^\dagger a_l, a_j^\dagger a_i \right] \middle| \Psi_0 \right\rangle$ on the right-hand-side is symmetric. Such a generalized eigenvalue problem has only real eigenvalues. The positive semi-definiteness of the double commutator matrix $\left\langle \Psi_0 \middle| \left[a_k^\dagger a_l, \left[H, a_j^\dagger a_i \right] \right] \middle| \Psi_0 \right\rangle$ for the exact ground state $\Psi_0 = \Psi^{\text{FCI}}$ follows from its variational optimality (Eq. (5)). For the same reason the double commutator matrix calculated from the variationally optimized 2DM is positive semi-definite [24]. Hence, both methods lead to real ERPA excitation spectra, whereas the usual RPA may suffer from unphysical imaginary eigenvalues.

The inclusion of ground-state correlation effects in the ERPA method makes it possible to describe the low-lying excited states of the atoms He to Ne in an adequate manner. The effect of including electron correlation can be measured by comparing:

- The error in the ERPA excitation energies for uncorrelated Hartree–Fock ground states – for which ERPA is equivalent to RPA – relative to the exact excitation energies in the same basis[2], $\Delta\epsilon_{\text{RPA}-\text{FCI}} \equiv \epsilon^{\text{HF}}_{\text{ERPA}} - \epsilon_{\text{FCI}}$; and
- The error in the ERPA excitation energies from the exact ground-state 2DM relative to the exact excitation energies in the same basis, $\Delta\epsilon_{\text{ERPA}-\text{FCI}} \equiv \epsilon^{\text{FCI}}_{\text{ERPA}} - \epsilon_{\text{FCI}}$.

The errors in the ERPA excitation energies are considerably smaller than those in the RPA excitation energies in most cases (Table 1). The ERPA spectra calculated from the exact 2DM for the Ne atom is significantly better than the RPA spectrum (Table 2). Even for excitations to partially-filled p-orbitals in the atoms B–F, the ERPA computed from the exact 2DM does relatively well (Tables 1 and 3).

Table 2
The excitation spectrum of Ne (in eV) computed with the ERPA method from variationally optimized 2DM's, $\epsilon^{\text{v2DM}}_{\text{ERPA}}$, agrees well with the ERPA spectrum from exact 2DM's, $\epsilon^{\text{FCI}}_{\text{ERPA}}$, and the exact spectrum, ϵ_{FCI}. The RPA neglects correlation and gives significantly poorer excitation energies ϵ_{RPA}.

		$\epsilon^{\text{v2DM}}_{\text{ERPA}}$	$\epsilon^{\text{FCI}}_{\text{ERPA}}$	ϵ_{RPA}	ϵ^{FCI}
$2s^2 2p^6$	^1S	0.000	0.000	0.000	0.000
$2s^2 2p^5 3s^1$	^3P	18.431	18.479	19.350	18.004
$2s^2 2p^5 3s^1$	^1P	18.975	19.022	20.096	18.470
$2s^2 2p^5 3p^1$	^3S	19.540	19.587	20.281	19.155
$2s^2 2p^5 3p^1$	^3D	20.193	20.254	21.162	19.754
$2s^2 2p^5 3p^1$	^1D	20.420	20.494	21.558	19.937
$2s^2 2p^5 3p^1$	^3P	20.467	20.546	21.568	20.007
$2s^2 2p^5 3p^1$	^1P	20.512	20.575	21.568	20.036
$2s^2 2p^5 3p^1$	^1S	21.971	22.073	23.472	21.386

The electron correlation effects present in the variationally optimized 2DM lead to qualitatively correct ERPA spectra for He-Be and Ne, but the spectra for B–F are poor. For the atoms B–F, the differences $\Delta\epsilon^{\text{v2DM}-\text{FCI}}_{\text{ERPA}} \equiv \epsilon^{\text{v2DM}}_{\text{ERPA}} - \epsilon^{\text{FCI}}_{\text{ERPA}}$ between the ERPA excitation energies computed from the variationally optimized 2DM and those computed from the exact 2DM, which are the best' excitation energies that can be obtained within the ERPA framework, are much bigger than the errors in the ground-state energies, $E_0^{\text{v2DM}} - E_0^{\text{FCI}}$ (Tables 1 and 4). Not only is the accuracy of the v2DM ERPA excitation energies for B–F poor, the spectrum is also qualitatively incorrect. While the low-energy spectra for Be (Table 5) and Ne (Table 2), for instance, are qualitatively correct, the spectrum for C is incorrect (Table 3). For all of the atoms Be-F, the lowest-energy excitations computed from the variationally optimized 2DM invariably correspond to a $2s \rightarrow 2p$ excitation, which is physically incorrect. In the C atom, the v2DM ERPA spectrum completely misses (or assigns an extremely high energy to) the low-energy excitations to the ^1D and ^1S states with the same predominant $2s^2 2p^2$ configuration as the ^3P ground state (Table 3). The origin of these problems must lie in the nature of the variationally optimized 2DM, since the ERPA spectrum computed from the exact 2DM is qualitatively correct.

More specifically, the ensemble nature of the variationally optimized 2DM leads to poor ERPA spectra. The 2DM that has been variationally optimized under the 2-positivity conditions has two main differences compared to the exact 2DM: it is not N-representable (and therefore not exact) and it represents an ensemble state. Whereas the exact 2DM's used here are pure states corresponding to the maximal spin projection of the ground spin state, the variationally optimized 2DM represents a spin-and angular momentum-averaged ensemble. Although the exact EOM would give the same results for different degenerate states and their ensembles, the ERPA method in general does not because the one-electron

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[2] In what follows, the notation ϵ_A^B denotes an excitation energy calculated using method A with as input the density matrix from method B. The input is not specified when obvious; the exact excitation energies are denoted ϵ_{FCI} and experimental results as $\epsilon_{\text{expt.}}$.

Table 3
The ERPA spectra of C (in eV) computed from exact 2DM's ($\epsilon^{\mathrm{FCI}}_{\mathrm{ERPA}}$) for different degenerate ground states are not consistent. The spectrum from the maximal spin projection agrees well with the exact spectrum (ϵ_{FCI}), but the spectra computed from ensembles of these degenerate states are particularly poor (the M_l and M_s components that are present in equal weights in the ensemble are listed in the second and third row). The ^{1}D and ^{1}S terms are even missing in some ensemble spectra. The ERPA spectrum computed from the spin-and angular momentum averaged ensemble of the exact 2DM's closely resembles the v2DM ERPA spectrum ($\epsilon^{\mathrm{v2DM}}_{\mathrm{ERPA}}$).

	$\epsilon^{\mathrm{FCI}}_{\mathrm{ERPA}}$									$\epsilon^{\mathrm{v2DM}}_{\mathrm{ERPA}}$	ϵ_{RPA}	ϵ_{FCI}	ϵ_{expt}
	M_l	0	1	0	1	0	−1, 0, 1	−1, 0, 1	−1, 0, 1				
	M_s	0	0	1	1	−1, 0, 1	0	1	−1, 0, 1				
$2s^22p^2$	^{3}P	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
$2s^22p^2$	^{1}D	1.332	1.332	1.260	1.260	1.962		1.659			1.311	1.486	1.264
$2s^22p^2$	^{1}S	3.013	3.013	1.882	1.882	1.962		3.620			0.511	2.932	2.684
$2s^12p^3$	^{5}S	7.497	7.497	4.041	4.041	7.508	9.204	6.409	10.277	11.250	1.687	3.935	4.183
$2s^12p^3$	^{3}D	10.660	10.660	6.662	6.662	10.665	12.620	11.901	12.620	13.925	4.370	8.322	7.946

Table 4
For the atoms B–F, the errors in the ground-state energies (in eV) of the variationally optimized 2DM relative to the exact 2DM, $E^{\mathrm{v2DM}}_0 - E^{\mathrm{FCI}}_0$, are considerably smaller than the errors in the first ERPA excitation energies of the variationally optimized 2DM relative to the exact 2DM, $\Delta\epsilon^{\mathrm{v2DM-FCI}}_{\mathrm{ERPA}}$.

	$E^{\mathrm{v2DM}}_0 - E^{\mathrm{FCI}}_0$	$\Delta\epsilon^{\mathrm{v2DM-FCI}}_{\mathrm{ERPA}}$
He	0.000	0.000
Li	−0.0048	0.005
Be	−0.0119	0.002
B	−0.4017	2.674
C	−0.8522	7.209
N	−0.8783	3.285
O	−1.6146	6.872
F	−1.5931	11.309
Ne	−0.4850	−0.047

Table 5
The excitation spectrum of Be (in eV) computed with the ERPA method from variationally optimized 2DM's, $\epsilon^{\mathrm{v2DM}}_{\mathrm{ERPA}}$, gives a qualitatively correct picture of the lowest-energy states of the Be atom, consistent with the ERPA results from exact 2DM's, $\epsilon^{\mathrm{FCI}}_{\mathrm{ERPA}}$, and the exact excitation energies ϵ_{FCI}.

		$\epsilon^{\mathrm{v2DM}}_{\mathrm{ERPA}}$	$\epsilon^{\mathrm{FCI}}_{\mathrm{ERPA}}$	ϵ_{FCI}	ϵ_{expt}
$2s^2$	^{1}S	0.000	0.000	0.000	0.000
2^1s2p^1	^{3}P	2.773	2.770	2.752	2.725
$2s^12p^1$	^{1}P	5.660	5.652	5.622	5.277
$2s^13s^1$	^{3}S	9.599	9.596	9.586	6.457
$2s^13s^1$	^{1}S	10.742	10.724	10.662	6.779

description of the excitations does not cover the whole spin-or angular momentum space. The ERPA spectra computed from exact 2DM's for different M_s or M_l states may thus be significantly different. This problem also occurs in RPA and TDDFT, and may be solved using techniques that are beyond the scope of this paper [25,26]. In practice, such techniques are not often applied because the excitation energies computed from the maximal spin projection often give fair results (Table 3). Ensemble ground states, however, are much more problematic. For instance, the ERPA excitation energies for the C atom computed from the spin-and angular momentum-averaged ensemble of exact 2DM's are much higher than those computed from any of the pure states. Moreover, the two lowest excitation energies are absent in the ensemble spectrum. The spin and angular momentum-averaged ensemble thus closely resembles the v2DM ERPA spectrum. The remaining differences are due to the N-representability errors in the variationally optimized 2DM. The ensemble nature of the variationally optimized 2DM therefore explains the large errors in the ERPA excitation energies for the atoms B, C, N, O and F. The good results for Li are an exception, because the one-electron description of the excited states is a good approximation in this case.

5. Conclusions

The ERPA equations make it possible to compute excitation energies from a correlated ground-state 2DM by assuming that the excited states are generated by one-electron excitations from the ground state. This type of approach is useful for density matrix methods, such as the v2DM method, because they typically only have a ground-state density matrix available. Optimizing a 2DM for an excited state by the same variational procedure would require special N-representability conditions to ensure the 2DM corresponds to a proper excited state, for which no practical conditions are known. The ERPA not only circumvents this theoretical problem by extracting excitation energies directly from the ground-state 2DM, but is also computationally more efficient than a direct approach.

The inclusion of ground-state correlation in ERPA in general leads to better excitation energies than the RPA. The ERPA spectra computed from correlated 2DM's for the Ne atom are significantly better than the RPA spectrum. Although the ERPA spectra for the open-shell atoms B, C, N, O and F depend on the angular momentum and spin projection of the ground state, the ERPA spectra computed from the exact 2DM's for the highest spin projection give a qualitatively correct picture of the excitations to the partially filled p-orbitals in these atoms. These findings justify the use of correlated density matrices as input for EOM-type methods. However, two main difficulties arise when the density matrices that are used as input to the ERPA are not derived from a wavefunction. First of all, unless the 2DM corresponds to a variational optimum, its ERPA spectrum may contain imaginary eigenvalues. The variational optimality of the v2DM method guarantees that the double-commutator matrix in the ERPA Eq. (1) is positive semi-definite and hence that the ERPA spectrum is real. When a 2DM from different origin is used, positivity of the double-commutator matrix can perhaps be imposed as a constraint or by construction to obtain a real spectrum. Secondly, the 2DM's from density matrix methods typically correspond to an ensemble of states, which may produce poor and qualitatively incorrect ERPA spectra. This is why the v2DM ERPA excitation energies are good for He, Li, Be and Ne, but poor for the atoms B–F. The excitation spectrum for the atoms B–F is not only inaccurate, but also qualitatively incorrect: the lowest-energy excitation invariably corresponds to a 2s → 2p excitation and low-lying states that are present in the ERPA spectrum computed from the exact pure state 2DM are missing. This is ultimately a consequence of the N-representability problem, since pure state N-representability is an even more complex problem than the ensemble N-representability that is usually pursued in density matrix methods.

To conclude, the ERPA method is a good starting point for further refinements, as higher-order excitations must be included to reach chemical accuracy, but is most suitable for pure ground-state matrices that lead to a positive semi-definite double commutator matrix.

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