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# Multiconfiguration Wave Functions for Highly Excited States by the Generalized Brillouin Theorem Method

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## Abstract

A multiconfiguration method is presented which can yield upper bounds to the energies of excited states within the single- or many-configuration approximation, and which shows quadratic convergence behavior. As an example, test calculations on valence and core excited states of the Li atom are discussed. The method is then applied to investigate molecular hole states. (1) Two kinds of correlation effects occur in core hole states of symmetrical molecules: in addition to the already known correlation effect, polarization of the valence shell by a localized hole, there is still another kind of correlation effect, core-core reorganization, of the order of about 1 eV. (2) When the analogous core model is used to interpret core excited states, three corrections have to be taken into consideration: in addition to the difference in ground-state geometries and the difference in exchange interactions, one must also correct for the difference in screening of the cores.

## 1. Introduction

Although the Hartree-Fock approach is quite suitable for the calculation of properties like equilibrium geometries or charge densities, it is usually insufficient for the calculation of transition energies and intensities. However, for electronic excitations from inner core to empty molecular orbitals outside the valence shell, we expect that Hartree-Fock calculations can be used to predict correct excitation energies because the inner shell pair correlation energy involved is nearly constant. The single configuration approximation should be sufficient in most cases when we are interested in term values of core excitations. With term values we mean the energetic distances of the excited states from the corresponding ionization limit.

However, the usual RHF routine [1] often suffers from severe difficulties. First it is sometimes not easy to achieve convergence, especially when two core orbitals have nearly the same orbital energy. Second it may lead to variational collapse [2] in the case of highly excited core hole states. And finally it cannot account for the correlation effect which may cause significant deviations from the HF prediction in special cases. All these problems can be tackled successfully by the Brillouin theorem method.

In the next section we will present a recently developed version of the so-called generalized Brillouin theorem (GBT) single- and multiconfiguration method, which is specially suitable for the calculation of (highly) excited states. Using the lithium atom as a very simple example we will show how this method works in the case of lower valence excited states, as well as higher core excited states. In Section 3 we will investigate the problem of inner shell holes in symmetrical molecules with equivalent nuclei by means

of the GBT method. Finally in Section 4 we will discuss the recently recorded XUV spectrum of the LiF molecule within the framework of the core analogy model. Special emphasis is laid on the discussion of the limitations of this model.

## 2. A GBT-MC Method for Excited States

The determination of the multiconfiguration wave function

$$\Psi = \sum_{v=1}^n c_v \cdot \gamma_v(\sigma_i) \quad (1)$$

consists of three steps. (a) Select a set of basis AOs, construct starting MOs  $\sigma_i$  from them, and then form a small set of configurations  $\gamma_v(\sigma_i)$ . (b) Optimize the linear coefficients  $c_v$ . (c) Improve the MOs  $\sigma_i$ . Steps (b) and (c) are repeated until convergence is reached.

Step (b) results in the standard eigenvalue problem of a limited CI expansion (MC or  $nC$  problem). According to the Hylleraas-Undheim theorem [3] the  $m$ th root  $\Psi^m$  of the MC secular equation is an upper bound to the energy of the  $m$ th state. In order to obtain a reasonable upper bound, one should therefore include representative configurations for all the  $m-1$  lower states in the  $nC$  expansion of Equation (1). However, not all of them have to be considered, as will be shown below.

The orbital optimization in step (c) can be performed by different techniques, which have been reviewed in a very recent paper by Grein and Banerjee [4]. We present here another method which is based on the generalized Brillouin theorem (GBT) [5] and is closely related to the GBT methods of Grein and others [6-8].

To illustrate our method we give a simple example of an excited state calculation using the two-configuration (2C) wave function  $\Psi^2 = c_1 \gamma_1(\sigma_i) + c_2 \gamma_2(\sigma_i)$ . In order to improve the occupied MOs  $\sigma_i$  by some admixture of other orbitals  $\sigma_a$ ,

$$\sigma_i' = \sigma_i + \delta \cdot \sigma_a$$

one has to search for that mixing parameter  $\delta_0$  which minimizes the second root  $E^2(\delta)$  of our 2C problem. Therefore we have the following necessary condition:

$$\frac{d}{d\delta} E^2(\delta) \Big|_{\delta=\delta_0} = 0 \quad (2)$$

It can be shown by a lengthy but straightforward derivation that up to second order in  $\delta$  Equation (2) is equivalent to the following so-called super-CI (SCI) problem:

$$\begin{pmatrix} \langle \Psi^2 | H - E | \Psi^2 \rangle & \cdot & \cdot \\ \langle \Psi_{ia}^2 | H - E | \Psi_{ia}^2 \rangle & & \cdot \\ \langle \Psi_{ia}^2 | H - E | \Psi^2 \rangle & + \langle \Psi_{ia^2}^2 | H - E | \Psi^2 \rangle & \cdot \\ \langle \Psi^1 | H - E | \Psi^2 \rangle = 0 & + \langle \Psi^1 | H - \cdot | \Psi_{ia}^2 \rangle & \langle \Psi^1 | H - E | \Psi^1 \rangle \end{pmatrix} \begin{pmatrix} 1 \\ \delta_0 \\ \eta \end{pmatrix} = 0 \quad (3)$$

with  $E \approx E^2(\delta_0)$ . The singly substituted MC functions  $\Psi_{ia}^m$  are given by

$$\Psi_{ia}^m = \sum_{v=1}^n c_v [\gamma_v(\sigma_i \rightarrow \sigma_a) - \gamma_v(\sigma_a \rightarrow \sigma_i)]$$

TABLE I. Excitation energies of Li, in electronvolts.

state	1C or 2C approx- imation	singly deexcited configs.	addit. lower configs.	resulting energy increase	nonext. correlat. configs.	calc.	emp. [10]	total excit.	
						nonext. correl. energy	extern. correl. energy	calc.	exp. [11]
$1s^2 3s^2 S$	3.33	$1s^2 2s$	—	0.00	—	0.00	0.0 <sub>5</sub>	3.4	3.32
$1s 2s^2 2S$	56.82	$1s^2 2s$	$1s^2 ns$	<0.01	$1s 2p^2$	-1.30	1.2	56.7	56.39
$\begin{smallmatrix} s & t \\ 1s & 2s & 2p \end{smallmatrix} 2P's$	56.87	$(1s^2-2s^2) 2p$	$1s^2 2p$	1.36	$1s 2p 3d$	-0.14	0.9	59.0	58.91
$\begin{smallmatrix} t & s \end{smallmatrix}$	60.53			0.15		-0.89	0.6 <sub>5</sub>	60.4 <sub>5</sub>	60.40

$\Psi_{i2a^2}^m$  denotes the corresponding doubly substituted MC functions. According to the GBT, the following relation holds for a fully optimized MC function  $\Psi^m$ :

$$\langle \Psi^m | H - E | \Psi_{ia}^m \rangle = 0$$

so that for the optimal occupied orbitals  $\sigma_i^{\text{opt}}$  the corresponding mixing parameter  $\delta_0$  becomes zero, since the first row and column of the SCI-matrix then vanish.

The upper left part of the SCI matrix, which is calculated from the MC wave function to be optimized ( $\Psi^2$ ) and from the corresponding singly substituted wave functions ( $\Psi_{ia}^2$ ), is the matrix used in the conventional GBT method for ground states [6, 7]. However, the elements of our SCI matrix contain additional integrals in order to achieve quadratic convergence. These additional integrals are formally obtained from the original ones by transfer of a single substitution from the ket to the bra and usually represent only a small correction. The lower state MC wave function  $\Psi^1$  in the SCI matrix plays the role of a projection operator which guarantees the upper boundedness of  $E$  in the orbital improvement process by preventing the mixing in of the lower state component. This new version of the GBT method shows quadratic convergence behavior even in the case of excited states having nearly degenerate MC roots and is free from the root flipping difficulty. We mention that the MC-GBT Equation (3) is very similar to an MC-SCF equation by Das and coworkers [9].

Table I gives results of some test calculations on a very simple system, the Li atom. The ground state,  $1s^2 2s^2 S$ , has been chosen as the zero level of energy. The first excited state of the same symmetry is  $1s^2 3s^2 S$ . As the  $3s \rightarrow 2s$  single substitution already represents the ground state in the SCI problem, it is not necessary to include the lowest MC root separately in Equation (3). Furthermore, the 2C wave function  $\Psi = c_1 |1s^2 2s| + c_2 |1s^2 3s|$  can always be transformed to a single determinant by a unitary transformation of the orbitals. Consequently there is no necessity to form an MC wave function consisting of such redundant lower state configurations. In general the GBT procedure yields single-configuration wave functions for excited states which are noninteracting with all lower singly deexcited configurations.

The lowest core hole state is the  $1s 2s^2 2S$ . The lower  $1s^2 2s$  state is obtained by a single deexcitation from  $2s$  to  $1s$ . However, the orthogonality constraints to all the other lower  $1s^2 ns$  states ( $n > 2$ ) are not yet included. Taking account of a few such configurations and performing a multi- instead of a single-configuration calculation raised the energy insignificantly, that is, by less than 0.01 eV. We take this result as further support for omitting also all those lower configurations from the MC expansion which differ strongly in spatial extent from the state under consideration.

Finally we discuss the configuration  $1s 2s 2p^2 P$ . There exist two different spin cou-

plings. The lower of the two  $^2P$  states has the  $2s$  and  $2p$  mainly coupled to a triplet and the  $1s$  and  $2s$  mainly to a singlet, as indicated in Table I. For the higher state the situation is just reversed. According to the Brillouin theorem [5] the  $2s \rightarrow 1s$  substitution gives rise to a mixed configuration  $(1s^2 2p - 2s^2 2p)^2P$  which is higher than either of the two  $^2P$  excited states under consideration. Therefore it is necessary to include the  $1s^2 2p$  configuration explicitly in the MC ansatz in order to prevent variational collapse. The lower  $^2P$  with the two  $s$  electrons mainly coupled to a singlet interacts strongly with  $1s^2 2p$  and is raised by 1.36 eV thereby.

Finally we have also included the nonexternal correlation configurations and added the semiempirical external correlation energy increments of Sinanoğlu [10] to the MC energies. When comparing these final test calculation results with the experimental excitation energies of Li in the last two columns of Table I, one must be reminded that our AO basis set defect is about 0.1 eV. With this point in mind the consistent agreement is remarkable. Further details on the GBT method and results of other test calculations will be published elsewhere [12].

### 3. Core Hole States in Symmetrical Molecules

We will use the  $K$  shell ionized  $\text{Li}_2$  molecule as the simplest example for the discussion of the underlying problem. The  $1s$  ionization potential (IP) obtained in the single configuration approximation is 64.68 eV. At first one might expect that this IP value will differ from the correct value mainly by the  $1s^2$  correlation energy of 1.2 eV (65.9 eV). However, MC calculations for  $\text{Li}_2^+$  [13] using a flexible enough wave function give 62.55 eV for the IP. This shows that the correlation energy of the molecular ion is about 3.3 eV larger than expected. According to our calculations this 3-eV difference comes mainly from two types of correlation effects.

First there is the effect usually called "polarization of the valence shell by a core hole localized on one of the two equivalent atoms," which has recently been discussed by Denis and coworkers [14]. In the framework of the excitonic picture [15] this correlation effect can be taken into account by an MC wave function using *equivalent* localized MOs:

$$\Psi_{vc}^{\text{loc}} = (1 + I)(|s_a s_b^2 \sigma^2| + c \cdot |s_a s_b^2 \sigma \sigma|)$$

where  $I$  refers to the inversion operator,  $s_a$  and  $s_b$  are the  $1s$  AOs on the left and right Li atom, and  $\sigma$  denotes valence shell MOs. A nearly equivalent but slightly more flexible representation with symmetry MOs is obtained by adding the  $(s_u \rightarrow s_g, \sigma_g \rightarrow \sigma_u)$  doubly excited configurations to the main configuration:

$$\Psi_{vc}^{\text{sym}} = |s_g s_u^2 \sigma_g^2| + c \cdot |s_g^2 s_u \sigma_g \sigma_u| \quad (4)$$

With the latter wave function (4) we obtained an energy lowering of  $\Delta E_{cv} = 2.54$  eV for this core-valence correlation.

There still remains a discrepancy of about 0.8 eV. We again start the discussion with the excitonic picture, where a localized  $1s$  core hole oscillates between the left and right Li atom. It is evident that we should use slightly different (nonorthogonal!)  $1s$  orbitals for the singly and doubly occupied core shells:

$$\Psi_{cc}^{\text{loc}} = |s_a' \tilde{s}_b^2 \sigma_g^2| + |s_b' \tilde{s}_a^2 \sigma_g^2| \quad (5)$$

According to Slater's rules,

$$s_a', s_b' \sim e^{-Z \cdot r}, \quad \tilde{s}_a, \tilde{s}_b \sim e^{-(Z-\alpha)r}$$

with  $\alpha = 0.30$ . However, in the canonical SCF wave function

$$\Psi_0^{\text{sym}} = |s_g s_u^2 \sigma_g^2|$$

or in the equivalent wave function with localized equivalent core orbitals,

$$\Psi_0^{\text{loc}} = |s_a s_b^2 \sigma_g^2| + |s_b s_a^2 \sigma_g^2|$$

both the singly and doubly occupied core orbitals take the same exponential parameter which will be the weighted mean of  $s'$  and  $\tilde{s}$  from wave function (5):

$$s \sim e^{-(Z-2\alpha/3)r}$$

According to this analysis one may estimate the energy lowering due to the core-core reorganization or correlation of wave function (5) to be

$$\Delta E_{cc} \approx \frac{1}{3} \alpha^2 \text{ a.u.} \approx 0.9 \text{ eV}$$

Here  $\Delta E_{cc}$  is independent of the nuclear charge. In the picture of symmetry MOs this effect can be described, instead, by  $s \rightarrow s^*$  single excitations combined with  $s_u^2 \rightarrow s_g^2$  double excitations:

$$\Psi_{cc}^{\text{sym}} = |s_g s_u^2 \sigma_g^2| + c_1 \cdot |s_g s_u s_u^* \sigma_g^2| + c_2 \cdot |s_g^* s_u^2 \sigma_g^2| + c_3 \cdot |s_g^* s_g^2 \sigma_g^2| \quad (6)$$

The  $s^*$  core orbitals have a node in the core region. The correlation energy accounted for by wave function (6) amounts to  $\Delta E_{cc} = 0.91 \text{ eV}$ .

Of course the two core-core and core-valence correlation effects are not additive. Instead of using a rather large MC function, which should also include the mixed substitutions corresponding to wave functions (4) and (6) in order to account simultaneously for both core-valence polarization and core-core reorganization, a much simpler approach is recommended. This is the well-known method of relaxing the  $g-u$  symmetry of the total wave function [16]. The above functions are all of the  $g$  type. From the corresponding  $u$ -type functions we obtain a  $^2\Sigma_g^- - ^2\Sigma_u$  splitting of only 0.04 eV. Therefore relaxing the  $g-u$  symmetry of the stationary Born-Oppenheimer electronic function should give a meaningful result. The single determinantal nonsymmetry wave function

$$\Psi = |s_a \tilde{s}_b^2 \sigma_a^2| \quad (7)$$

has the following characteristics. The two nonequivalent localized core orbitals  $s_a$  and  $\tilde{s}_b$  can conveniently take into account the core-core correlation effect, and  $\sigma_a$  is a slightly more delocalized valence orbital which can account for the core-valence correlation. The energy lowering obtained by relaxing the symmetry is 3.18 eV. This is 8% smaller than the direct sum of  $\Delta E_{cv}$  and  $\Delta E_{cc}$ . The remaining discrepancy between the calculated 3.18 and the above-mentioned 3.3 eV is due to a change of intravalence correlation upon core ionization.

The  $^2\Sigma_g^- - ^2\Sigma_u$  energy splitting of 0.04 eV corresponds to an "exchange frequency of the localized hole" of the order of  $10^{13} \text{ sec}^{-1}$ , which is comparable to the vibrational frequency, and also to the lifetime of the hole state. Koopmans' theorem failed in predicting the  $g-u$  splitting of the IP:  $\epsilon_u - \epsilon_g$  is only 0.01 eV. This large discrepancy was reproduced at different levels of sophistication of our calculations.

#### 4. Interpretation of Core Excitation Spectra: The Core Analogy Model

In the core analogy model [17] one assumes that the interaction of a valence electron with an atomic core having one electron hole is comparable to that with a complete core

TABLE II. Term values\* of BeF and Li core excited LiF.

orbital of optical electron	experimental		calculated		BeF - LiF		calculated contribution due		
	vertical		vertical		difference		to differences in		
	term values		term values				bond	exchange	effective Z
	BeF [18]	LiF [19]	BeF	LiF	exp.	calc.	length		
column	1	2	3	4	5	6	7	8	9
$\sigma^*$	9.1	8.6	9.3	7.8	-0.5	-1.5	+0.3	-0.9	-0.8
$\pi^*$	5.0	6.1	4.8	5.1	1.1	0.3	+0.5	-0.4	+0.2
$\sigma^* - \pi^*$	4.1	2.5	4.5	2.7	-1.6	-1.8	-0.2	-0.5	-1.0
3s	2.95	3.0			± 0.1				
3p <sub>σ</sub>	2.85								
3p <sub>π</sub>	(2.0)								

\*Term value = distance of excited state to ionization limit.

but having one proton more in the nucleus. This model has successfully been applied to a variety of molecules. However, in recent investigations significant discrepancies have been discovered demonstrating that several corrections have to be taken into account. The LiF molecule is specially suited to serve as an example.

The core analog of the Li 1s-excited Li\*F is the BeF molecular radical. Above the occupied orbitals there are two valence orbitals  $\sigma^*$  and  $\pi^*$  and a series of molecular Rydberg orbitals available for the optical electron of Li\*F or BeF. The corresponding vertical term values of BeF and Li\*F are given in the first columns of Table II. One can see large discrepancies in the case of the two valence levels. On the basis of hole state calculations, which will be published elsewhere [13], these discrepancies can be attributed to three sources.

(1) The vertical term values refer to ground-state geometries, which are quite different for BeF ( $R = 1.36 \text{ \AA}$ ) and LiF ( $R = 1.56 \text{ \AA}$ ), mainly due to the different ionic core radii of  $\text{Be}^{2+}$  and  $\text{Li}^+$ . Since the two valence orbitals, especially the  $\pi^*$  one, are strongly antibonding, their term values will decrease considerably when the bond length of LiF is diminished to the BeF value (see column 7 of Table II).

(2) For the doublet states of BeF the exchange interaction of the unpaired electron  $v$  with the Be 1s<sup>2</sup> shell is  $-K$ , where  $K$  is the exchange integral of the 1s AO and the optical orbital  $v$ . On the other hand, for the singlet and triplet states of Li\*F the exchange interaction of the excited electron  $v$  with the Li\* 1s shell is  $+K$  and  $-K$ , respectively. Since the experimental term values of Li\*F refer to the singlet states, the BeF term values should be larger than those of Li\*F by the singlet-triplet splittings of the latter molecule. The corresponding data in column 8 of Table II show that the splitting is rather large for the penetrating  $\sigma^*$  orbital.

(3) To first order of approximation the  $Z$  1s and the  $(Z + 1)$  1s<sup>2</sup> cores act as Coulombic charges of magnitude  $Z - 1$ . However, the incomplete shielding by the 1s electrons results in larger effective nuclear charges and consequently in larger term values for the  $Z + 1$  analog, at least for penetrating orbitals like  $\sigma^*$  (see column 9 of Table II). Model calculations have shown that this difference decreases quickly with increasing  $Z$  and is only appreciable for the rather extended  $K$  shells of the very light elements.

All three effects tend to decrease the  $\sigma^* - \pi^*$  splitting of core excited Li\*F relative to BeF and explain at least qualitatively the experimental findings.

## 5. Conclusion

Our modification of the conventional Brillouin theorem method has proven quite successful in the calculation of energy-bounded single- and multiconfigurational wave functions for (highly) excited states. Wave functions of such simple structure are very instructive to give a deeper insight into physical problems. Two examples of this kind from the field of core excitation phenomena have been given in this note and are summarized in the abstract. However, one main disadvantage of the method should not be concealed. In fact the energy has usually converged within  $10^{-3}$  eV after about five iterations in the case of short MC expansions, but each iteration step requires a large computational effort for the transformation of the two-electron integrals and for the building up of the SCI matrix.

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