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# Atomic radiative transition probabilities using negative-energy orbitals in fully variational wave functions

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## Abstract

Transition probabilities have been computed using a variational many-electron theory [R. Jáuregui, C.F. Bunge, E. Ley-Koo, Phys. Rev. A 55 (1997) 1781] incorporating positive-energy and negative-energy orbitals without ambiguities, and absolutely free from variational collapse. The results agree with experiment and with other calculations based on the no-pair Hamiltonian where ad hoc negative-energy orbitals occur in first-order corrections to the wave functions. © 2005 Elsevier B.V. All rights reserved.

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## 1. Introduction

Relativistic electronic structure calculations are approached either (a) with a relativistic Hamiltonian  $H$  based on Dirac's one-electron Hamiltonian and suitable two-body terms [1], or (b) with the conventional Breit-Pauli Hamiltonian  $H_{BP}$  [2] and improved versions [3]. In (b), negative-energy orbitals cannot be included, while in (a) these can be incorporated perturbatively into the wave func-

tions [4]. In any case, a full configuration interaction (CI) expansion and approximations thereon need to be considered.

In (a), the complete Hamiltonian  $H$  is not bounded from below, then the usual variational theorem does not hold. One way out is to project  $H$  into a representation incorporating only positive-energy orbitals. Let  $h_0$  be a one-electron operator constructed out of four by four Dirac matrices,

$$h_0(1)u_n^+(1) = \epsilon_n u_n^+(1), \quad \epsilon_n > 0, \quad (1)$$

$$h_0(1)u_n^-(1) = \epsilon_n u_n^-(1), \quad \epsilon_n < 0, \quad (2)$$

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with positive-energy solutions  $u_n^+$  as well as negative-energy ones  $u_n^-$ . A one-particle projection operator into positive-energy orbitals,  $\lambda^+(1)$ , can be used to construct an N-particle projection operator  $A^{++}$ ,

$$\lambda^+(1) = \sum_{n(\epsilon_n > 0)} |u_n^+(1)\rangle \langle u_n^+(1)|, \quad (3)$$

$$A^{++} = \prod_{i=1}^N \lambda^+(i), \quad (4)$$

and the complete Hamiltonian  $H$  gets truncated into the “no-pair” Hamiltonian  $H^+$ ,

$$H^+ = A^{++} H A^{++}, \quad (5)$$

$$H^+ \Psi_i^+ = E_i^+ \Psi_i^+. \quad (6)$$

Because  $h_0$  is not unique, positive- and negative-energy orbitals have some degree of arbitrariness. In a finite-size orbital representation,  $H^+$  is given by a bounded and hermitian matrix  $\mathbf{H}^+$  of order  $\mathcal{N}^+$ , satisfying the CI-matrix eigenvalue equations:

$$\mathbf{H}^+ \mathbf{C}_i^+ = E_i^+ \mathbf{C}_i^+ \quad i = 1, 2, \dots, \mathcal{N}^+, \quad (7)$$

where  $\mathcal{N}^+$  is equal to the size of the full CI expansion.

We now come back to the original Hamiltonian  $H$  and consider its complete representation in an orbital basis incorporating both positive-energy and negative-energy orbitals:

$$\mathbf{H} \mathbf{C}_k = E_k \mathbf{C}_k \quad i = 1, 2, \dots, \mathcal{N} = \mathcal{N}^- + \mathcal{N}^+, \quad (8)$$

where, in general,  $\mathcal{N}$  greatly exceeds  $\mathcal{N}^+$ .

Orbitals do not need to be classified into positive-energy and negative-energy ones. One may start with any set of variously scaled Dirac eigenfunctions. Then this orbital basis is enlarged by an equal number of bispinors where the sign of the lower component is changed, so that the full basis is invariant upon separate linear transformations among the upper and lower components, respectively, and therefore (8) has unique solutions.

Let us now study the relationship between Eqs. (7) and (8). To do that we introduce an hermitian eigenproblem of order  $m$ ,

$$\mathbf{A}^{(m)} v_j = \mu_j^{(m)} v_j, \quad j = 1, 2, \dots, m. \quad (9)$$

After bordering  $\mathbf{A}^{(m)}$  with an extra row and column to produce another hermitian matrix  $\mathbf{A}^{(m+1)}$ , if the eigenvalues  $\mu_j^{(m)}$  and  $\mu_j^{(m+1)}$  are in nondecreasing order, it holds [5]

$$\mu_j^{(m+1)} \leq \mu_j^{(m)} \leq \mu_{(j+1)}^{(m+1)} \leq \dots \quad (10)$$

By considering increasingly larger hermitian matrices up to order  $m + p$  we get, as a corollary to the above:

$$\mu_j^{(m)} \leq \mu_{(j+1)}^{(m+1)} \leq \mu_{(j+2)}^{(m+2)} \leq \dots \mu_{(j+p)}^{(m+p)} \leq \dots \quad (11)$$

Setting  $j = i$ ,  $m = \mathcal{N}^+$  and  $p = \mathcal{N}^-$ , we get

$$E_i^+ \leq E_{i+\mathcal{N}^-}, \quad i = 1, 2, \dots, \mathcal{N}^+, \quad (12)$$

guaranteeing that after jumping over  $\mathcal{N}^- = \mathcal{N} - \mathcal{N}^+$  states, the eigenvalues of  $\mathbf{H}$  are rigorous upper bounds to the eigenvalues of  $\mathbf{H}^+$  [6]. Departing from full CI, the above theorem can be applied to obtain multiconfiguration SCF wave functions [7], and other goodies [8–11].

Eq. (8) contains two sets of equations with different behavior:

$$\mathbf{H} \mathbf{C}_k = E_k \mathbf{C}_k \quad k = 1, 2, \dots, \mathcal{N}^-, \quad (13)$$

$$\mathbf{H} \mathbf{C}_{i+\mathcal{N}^-} = E_{i+\mathcal{N}^-} \mathbf{C}_{i+\mathcal{N}^-} \quad i = 1, 2, \dots, \mathcal{N}^+. \quad (14)$$

In Eq. (13), although the  $\mathbf{C}_k$  represent  $\mathcal{N}$  linear variational coefficients, neither these nor  $E_k$  can be made stable upon variations in the nonlinear parameters specifying the one-particle basis. Thus, even if Eq. (13) is mathematically correct, variational collapse towards minus infinity ensues after legitimate variations in the basis set (within Hilbert space).

On the other hand, according to (12),  $E_{i+\mathcal{N}^-}$  is bounded below by  $E_i^+$  thus Eq. (14) yields solutions which are stable upon *any* variations in the basis set. Therefore, after jumping over the lowest  $\mathcal{N}^-$  eigenvalues of Eq. (8) we do find a genuine variational theorem valid for the remaining  $\mathcal{N}^+$  higher-lying eigenvalues encompassing the ground and all excited eigenstates. The theory behind Eq. (14) shall be called JBL theory [6].

Negative-energy orbitals are known to play a decisive role in some transition probabilities [12]. Extant calculations [4,12–16] involve many

methodologies, however, none of them incorporates negative-energy orbitals in a unique way as JBL theory does. Next we apply the JBL approach to calculate transition probabilities in He and He-like ions.

## 2. Transition probabilities calculated with JBL theory

Wave functions are calculated variationally by CI employing scaled hydrogenic Dirac-eigenfunctions as basis orbitals with scaling factors being energy-optimized in the framework either of the Dirac–Coulomb or of the Breit–Dirac–Coulomb Hamiltonian. Presently, a single orbital basis is used for each transition. The computer program [17] is general for any state of any atom [18] and multipolar electric and magnetic transition probabilities  $A_{ki}$ 's are evaluated using general and well known mathematical expressions [19]. Full CI will be assumed throughout.

In Table 1 we consider the magnetic dipole transition  $1s2s\ ^3S_1 \rightarrow 1s^2\ ^1S_0$  in He [20]. Our value for  $A_{ki}$  agrees well with other calculations. A rather large 28S24p24P20d20D16f16F12g12G8h8H

energy-optimized basis had to be employed (lower and upper case letters are for  $\ell-1/2$  and  $\ell+1/2$  orbitals, respectively). For He  $1s^2$ , the present basis yields  $\mathcal{N}^+ = 505$ ,  $\mathcal{N}^- = 1421$ , thus the first bound state is the eigensolution of order 1422. Neither positive-energy nor negative-energy orbitals are evaluated explicitly. Similar results for  $\text{Ar}^{16+}$  are reported in Table 2.

A more stringent test of JBL theory is through the M1 transition  $1s3s\ ^3S_1 \rightarrow 1s2s\ ^3S_1$  in He, reported in Table 3. Here the effect of negative-energy orbitals is known to be rather large [4,12]. Disagreement of ten percent between the Breit–Dirac–Fock perturbative treatment [4] and the JBL theory probably reflects the approximate nature of the perturbative framework as compared with the fully variational approach. In addition, the Breit–Pauli calculation [15] cannot include negative-energy orbitals, resulting in an  $A_{ki}$  value fifty percent too low.

Let us now consider the same transition for increasing nuclear charge. Since the ratio of negative- to positive-energy orbital contributions for M1 transitions with no spin change scales as the inverse of the nuclear charge [4], agreement between the perturbative and the variational theories

Table 1  
Comparison of calculated and experimental  $A_{ki}$  for  $1s2s\ ^3S_1 \rightarrow 1s^2\ ^1S_0$  in He

	$\Delta E$ (a.u.)	$\Delta E$ (cm <sup>-1</sup> )	$\lambda$ (Å)	$A_{ki}$ (10 <sup>-4</sup> s <sup>-1</sup> )
Experiment, [21]				1.10
This work	0.728234	159807	625.75	1.2732
This work <sup>a</sup>	0.728357	159833	625.65	1.2725
Calculation, [15]	0.728357	159833	625.65	1.2724
Calculation, [14]	0.728550	159877	625.48	1.266

<sup>a</sup> Transition energy from [15].

Table 2  
Comparison of calculated  $A_{ki}$  for  $1s2s\ ^3S_1 \rightarrow 1s^2\ ^1S_0$  in  $\text{Ar}^{16+}$

	$\Delta E$ (a.u.)	$\Delta E$ (cm <sup>-1</sup> )	$\lambda$ (Å)	$A_{ki}$ (10 <sup>6</sup> s <sup>-1</sup> )
Experiment, [22]				4.95(25)
This work	114.099604	25041624	3.9934	4.791
This work <sup>a</sup>			3.9941	4.790
Calculation, [14]			3.9941	4.787
Calculation, [13]	114.072		3.9943	4.776

<sup>a</sup> Transition energy from [14].

Table 3

Comparison of calculated  $A_{ki}$  for  $1s3s\ ^3S_1 \rightarrow 1s2s\ ^3S_1$  in He

	$\Delta E$ (a.u.)	$\Delta E$ (cm <sup>-1</sup> )	$\lambda$ (Å)	$A_{ki}$ (10 <sup>-8</sup> s <sup>-1</sup> )
This work	0.106547	23381.2	4276.94	1.2962
Calculation, [4]				1.17
Calculation, [15]				0.6485

Table 4

Comparison of calculated  $A_{ki}$  for  $1s3s\ ^3S_1 \rightarrow 1s2s\ ^3S_1$  for several nuclear charges  $Z$ 

	$Z$	$\Delta E$ (a.u.)	$\Delta E$ (cm <sup>-1</sup> )	$\lambda$ (Å)	$A_{ki}$ (s <sup>-1</sup> )
This work	3	0.358694	78718.1	1270.36	4.9752 [-6]
Calculation, [4]	3				4.80 [-6]
This work	4	0.750518	164709.7	607.129	1.9307 [-4]
Calculation, [4]	4				1.90 [-4]
This work	5	1.281364	281213.0	355.602	2.7637 [-3]
Calculation, [4]	5				2.73 [-3]
This work	9	4.799699	1053381.7	94.9323	2.0359

Table 5

Comparison of calculated and experimental  $A_{ki}$  for  $1s2p\ ^3P_2 \rightarrow 1s^2\ ^1S_0$  in He

	$\Delta E$ (a.u.)	$\Delta E$ (cm <sup>-1</sup> )	$\lambda$ (Å)	$A_{ki}$ (10 <sup>-1</sup> s <sup>-1</sup> )
This work	0.770303	169038.9	591.580	3.2657
This work <sup>a</sup>	0.770560	169095.2	591.383	3.2711
Calculation, [15]	0.770560			3.2703
Calculation, [14]			591.33	3.271

<sup>a</sup> Transition energy from [15].

Table 6

Comparison of calculated and experimental  $A_{ki}$  for  $1s2p\ ^1P_1 \rightarrow 1s^2\ ^1S_0$  in He

	$\Delta E$ (a.u.)	$\Delta E$ (cm <sup>-1</sup> )	$\lambda$ (Å)	$A_{ki}$ (10 <sup>8</sup> s <sup>-1</sup> )
This work <sup>a</sup>	0.779587	171076.2	584.535	1.79694
This work <sup>b</sup>				1.79692
This work <sup>c</sup>			584.25	1.79930
Calculation, [14]			584.25	1.799(9)

<sup>a</sup> Velocity form.<sup>b</sup> Length form.<sup>c</sup> Length form, transition energy from [14].

is expected to improve with increasing nuclear charge, as exhibited in Table 4. A typical magnetic quadrupole transition is given in Table 5. The resonance electric dipole transition in Table 6 shows a satisfactory agreement between velocity and length forms.

### 3. Conclusions

Although JBL theory was rigorously conceived from the outset [6] it has now acquired acceptable physical status after producing sensitive transition probability results very similar albeit not strictly equal to other results obtained with established theoretical approaches. So far, JBL is the only theory allowing full variational incorporation of negative-energy orbitals at the Hamiltonian level and in a way which is invariant upon any linear transformation between the starting orbitals, viz., without need to define positive-energy nor negative-energy orbitals explicitly and therefore avoiding sensitive dependence on the choice of the model potential in  $h_0$  [4]. As a byproduct, four by four Hamiltonians  $H$  are restored to full health [23] after being pronounced sick for several decades [24,25].

Very accurate predictions of transition probabilities will require some technical improvements (in progress): use of separately energy-optimized orbitals for each wave function (demanding non-orthogonal orbitals in calculations of matrix elements for transition probabilities), and direct calculation of highly excited eigenvalues and eigenvectors of order  $\mathcal{N} + i$  (with iterative rather than diagonalization methods). The incorporation of further terms into the Hamiltonian to make it more accurate is a continuous challenge to be attended on a permanent basis.

## References

- [1] I.P. Grant, in: G.W.F. Drake (Ed.), Atomic, Molecular and Optical Physics Handbook, AIP Press, New York, 1996, p. 258.
- [2] C.F. Fischer, in: G.W.F. Drake (Ed.), Atomic, Molecular and Optical Physics Handbook, AIP Press, New York, 1996.
- [3] K. Pachucki, Phys. Rev. A 67 (2003) 012504.
- [4] A. Derevianko, I.M. Savukov, W.R. Johnson, Phys. Rev. A 58 (1998) 4453.
- [5] H. Bateman, Bull. Am. Math. Soc. 18 (1912) 179.
- [6] R. Jáuregui, C.F. Bunge, E. Ley-Koo, Phys. Rev. A 55 (1997) 1781.
- [7] C.F. Bunge, R. Jáuregui, E. Ley-Koo, Can. J. Phys. 76 (1998) 421.
- [8] C.F. Bunge, R. Jáuregui, E. Ley-Koo, Int. J. Quant. Chem. 70 (1998) 805.
- [9] E. Ley-Koo, C.F. Bunge, R. Jáuregui, Teochem. 527 (2000) 11.
- [10] C.F. Bunge, E. Ley-Koo, R. Jáuregui, Mol. Phys. 98 (2000) 1067.
- [11] C.F. Bunge, E. Ley-Koo, R. Jáuregui, Int. J. Quant. Chem. 80 (2000) 461.
- [12] P. Indelicato, Phys. Rev. Lett. 77 (1996) 3323.
- [13] E. Lindroth, S. Salomonson, Phys. Rev. A 41 (1990) 4659.
- [14] W.R. Johnson, D.R. Plante, J. Sapirstein, Adv. At. Mol. Opt. Phys. 35 (1995) 255.
- [15] G. Lach, K. Pachucki, Phys. Rev. A 64 (2001) 042510.
- [16] P. Indelicato, V.M. Shabaev, A.V. Volotka, Phys. Rev. A 69 (2004) 062506.
- [17] Available upon request at bunge@fisica.unam.mx.
- [18] A.V. Bunge, C.F. Bunge, R. Jáuregui, G. Cisneros, Comp. Chem. 13 (1989) 201.
- [19] I.P. Grant, J. Phys. B 7 (1974) 1458.
- [20] G. Feinberg, J. Sucher, Phys. Rev. Lett. 12 (1971) 681.
- [21] H.W. Moss, J.R. Woodworth, Phys. Rev. A 12 (1975) 2455.
- [22] G. Hubricht, E. Träbert, Z. Phys. D 7 (1987) 243.
- [23] E. Ley-Koo, C.F. Bunge, R. Jáuregui, in: J.A. Heras, R.V. Jiménez (Eds.), Topics in Contemporary Physics, IPN, México, 2000, p. 33.
- [24] G.E. Brown, D.G. Ravenhall, Proc. Roy. Soc. London, A 208 (1951) 552.
- [25] J. Sucher, Phys. Rev. A 22 (1980) 348.