

Partitioning technique procedure revisited II: Application to the Stark and Zeeman problems in light atoms

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We show that the modified partitioning procedure can be applied to study the spherical and nonspherical Stark effect in the hydrogen atom and the spherical quadratic Zeeman effect in H^- , the helium atom and He-like ions: Li^+ , Be^{++} , etc. We present ground-state energy values for λ (in a.u.) in the interval $0.001 \leq \lambda \leq 0.2$ (a.u. = $5.142 \cdot 10^9$ volts/cm) and for magnetic field γ (in a.u.) in the interval $0.1 \leq \gamma \leq 1.0$ (a.u. = $2.353 \cdot 10^9$ gauss). We compare our results to values available in the literature; they are, in general, better than those obtained by other methods.

1. Introduction

The study of atoms in magnetic and electric fields is a subject of interest in atomic physics [8–10,12–14]. This problem has drawn the interest of many authors, not only because of its physical implications but also as a test bench for a great variety of approximate quantum methods [1,12–14,23].

Recently we have presented a reformulation of the partitioning procedure [20] and applied our equations (called modified partitioning procedure, MPP) to study the hydrogen atom in a strong magnetic field (Zeeman effect). Here, we apply the MPP equations to Stark problem in the hydrogen atom and to the spherical quadratic Zeeman effect in helium-like ions: H^- , He, Li^+ , Be^{++} , etc. So we extend the MPP to the case of two-electron systems and analyze its behavior in these new situations. The MPP is an analytic method and was developed to determine the eigenvalues and eigenkets of Schrödinger's equation explicitly. It differs from the original development of the partitioning approach in two aspects: (i) in the MPP the partitioning technique is applied directly to the auxiliary problem $\mathbf{H}_0|\varphi_l\rangle = E_l^0|\varphi_l\rangle$ ($\mathbf{H} = \mathbf{H}_0 + \mathbf{V}$), supposed resolved, and (ii) as reference ket the MPP uses the eigenket $|\Psi_l\rangle$ of \mathbf{H} instead of $|\varphi_l\rangle$. In consequence, differently from Löwdin's development [20,21], the reduced resolvent \mathbf{T}

in our approach does not depend on \mathbf{H} and we can obtain a set of nonlinear algebraic equations for the wave operator matrix elements \mathbf{w}_{sl} . Hence we can determine E_l directly in terms of \mathbf{w}_{sl} and \mathbf{V}_{sl} , potential matrix elements.

This paper is organized as follows: in section 2 we present a résumé of the modified partitioning procedure and apply to spherical and nonspherical Stark effect and to Zeeman effect. Section 3 contains our results and conclusions.

2. Modified partitioning procedure

The exact solution of an atom in electric or magnetic field consists, of course, in finding eigenvalues E_l and eigenkets $|\Psi_l\rangle$ of the equation

$$\mathbf{H}|\Psi_l\rangle = E_l|\Psi_l\rangle, \quad (1)$$

where

$$\mathbf{H} = \mathbf{K} + \mathbf{V}_0 + \mathbf{V} = \mathbf{H}_0 + \mathbf{V} \quad (2)$$

with \mathbf{K} – kinetic energy operator, \mathbf{V}_0 – electron–nucleus interaction operator, and \mathbf{V} – electron–electron and electron–external field interaction operators.

By the partitioning technique procedure we consider equation (1) and

$$\mathbf{H}_0|\varphi_l\rangle = E_l^0|\varphi_l\rangle \quad (3)$$

with $|\varphi_l\rangle$, E_l^0 known and $|\Psi_l\rangle$, E_l to be determined.

Using MPP (see [20] for details) we introduce the self-adjoint modified projection operators \mathbf{Q} and \mathbf{P} which define certain subspaces H_a and H_b , respectively, in the total Hilbert space H . They satisfy the relations

$$\mathbf{Q}^2 = c\mathbf{Q}, \quad \mathbf{Q}^+ = \mathbf{Q}, \quad \mathbf{QP} = \mathbf{PQ} = 0, \quad (4)$$

$$\mathbf{P}^2 = c\mathbf{P}, \quad \mathbf{P}^+ = \mathbf{P}, \quad \mathbf{P} = c - \mathbf{Q} \quad (5)$$

and are constructed as

$$\mathbf{Q} = |\Psi_l\rangle\langle\Psi_l|, \quad \mathbf{P} = c - |\Psi_l\rangle\langle\Psi_l| \quad (6)$$

with $c = \langle\Psi_l|\Psi_l\rangle$ and $H = H_a \oplus H_b$.

With the operators \mathbf{Q} and \mathbf{P} , we define the reduced resolvent

$$\mathbf{T} = \mathbf{P}[\alpha\mathbf{Q} + \mathbf{P}(\varepsilon - \mathbf{H}_0)\mathbf{P}]^{-1}\mathbf{P} \quad (7)$$

and the operator

$$\mathbf{w} = \mathbf{Q} + \mathbf{TH}_0\mathbf{Q}. \quad (8)$$

Then, we have, after some algebraic calculation, that

$$|\Psi_l\rangle = (1 - \mathbf{TV})^{-1}|\varphi_l\rangle = \mathbf{w}|\varphi_l\rangle \quad (9)$$

and

$$E_l = E_l^0 + \langle \varphi_l | \mathbf{V} \mathbf{w} | \varphi_l \rangle / \langle \varphi_l | \mathbf{w}^+ \mathbf{w} | \varphi_l \rangle. \quad (10)$$

Equations (9) and (10) are the fundamental relations of the modified partitioning technique. The problem of finding the eigenvalues E_l and the eigenkets $|\Psi_l\rangle$ from equations (9), (10), however, is not trivial one because it is necessary to know the modified wave operator matrix elements $\mathbf{w}_{sl} = \langle \varphi_s | \mathbf{w} | \varphi_l \rangle$, with $\mathbf{w} = (1 - \mathbf{T}\mathbf{V})^{-1}$. We adopt then the development presented in [20], that is, we consider the relations

$$\begin{aligned} \mathbf{w} &= 1 + \mathbf{T}\mathbf{V}\mathbf{w}, \\ \mathbf{P}(E_l^0 - \mathbf{H}_0)\mathbf{T} &= \mathbf{P}, \\ \langle \Psi_l | &= \langle \varphi_l | \mathbf{w}^+, \\ \sum_k |\varphi_k\rangle \langle \varphi_k | &= 1, \end{aligned}$$

where $\{|\varphi_k\rangle\} = \{|\varphi_1\rangle, |\varphi_2\rangle, \dots, |\varphi_l\rangle, \dots, |\varphi_s\rangle, \dots\}$ is the orthonormal complete set of eigenkets of \mathbf{H}_0 , and we obtain (if we use a finite set of eigenfunctions) for $l \neq s$ (l fixed and $s = 1, 2, \dots, N$) that

$$(E_l^0 - E_s^0)\mathbf{w}_{sl}\mathbf{w}_{ll} - \mathbf{w}_{ll} \sum_{k=1}^N \mathbf{V}_{sk}\mathbf{w}_{kl} + \mathbf{w}_{sl} \sum_{k=1}^N \mathbf{V}_{lk}\mathbf{w}_{kl} = 0 \quad (11)$$

with

$$\mathbf{w}_{ll} = \sum_{k=1}^N \mathbf{w}_{kl}^2. \quad (12)$$

Equations (11) and (12) constitute an algebraic system in the variables \mathbf{w}_{sl} . The number of equations in this system is equal to the number of variables \mathbf{w}_{sl} . As a consequence, we determine \mathbf{w}_{sl} and we write from equations (9) and (10) that

$$|\Psi_l\rangle = \sum_{k=1}^N \mathbf{w}_{kl} |\varphi_k\rangle, \quad (13)$$

$$E_l = E_l^0 + \sum_{k=1}^N \mathbf{V}_{lk}\mathbf{w}_{kl} / \mathbf{w}_{ll}, \quad (14)$$

where N is the number of eigenkets of \mathbf{H}_0 we have considered in the set $\{|\varphi_k\rangle\}$ and $\mathbf{V}_{lk} = \langle \varphi_l | \mathbf{V} | \varphi_k \rangle$.

Equations (13), (14) are the solution for equation (1) by the MPP technique. It is interesting to note that equation (14) is not a perturbative expansion in \mathbf{V} ; the value of E_l depends on the basis set $\{|\varphi_k\rangle\}$ chosen and the number N of basis functions used, only. This fact allows to study atoms in interaction with intense and super-intense fields.

In following subsection we discuss the application of MPP to Stark and Zeeman effects.

2.1. Modified partitioning procedure applied to Stark effect

We consider the spherical and nonspherical Stark effect in the hydrogen atom. In this case we have for \mathbf{V}_0 and \mathbf{V} in equations (1) and (2)

$$\mathbf{V}_0 = -\frac{1}{r}, \quad \mathbf{V} = \begin{cases} \lambda r \equiv \mathbf{V}_1 & \text{for the spherical Stark effect,} \\ \lambda r \cos \theta \equiv \mathbf{V}_2 & \text{for the nonspherical Stark effect.} \end{cases}$$

The set $\{|\varphi_k\rangle\}$ can be composed by the eigenfunctions of the hydrogen atom, that is (with the usual notation)

$$|\varphi_k\rangle \equiv |nlm\rangle = R_{nl}(r)Y_{lm}(\theta, \varphi) \quad (15)$$

with $n = 1, 2, \dots$, $l = 1, 2, \dots, n-1$, $-l \leq m \leq l$; but we can use also an arbitrary basis set, i.e.,

$$|\varphi_k\rangle \equiv |nlm, \alpha\rangle = P_{nl}(\alpha r)Y_{lm}(\theta, \varphi) \quad (16)$$

obtained from functions (15) using the transformation $1/n \rightarrow \alpha$, where α is a variational parameter to be determined for each value of λ .

Equations (11) and (12) are applied directly when we use the set of basis functions $\{|\varphi_k\rangle\}$ formed by the eigenfunctions of \mathbf{H}_0 . For the use of set (16), a little calculation shows that we have for E_l , as a function of α ,

$$E_l = \sum_{k=1}^N \left(\alpha^2 \mathbf{K}_{lk} + \alpha \mathbf{V}_{lk}^0 + \frac{1}{\alpha} \mathbf{V}_{lk} \right) \mathbf{w}_{kl}, \quad (17)$$

where \mathbf{K}_{lk} , \mathbf{V}_{lk}^0 and \mathbf{V}_{lk} are matrix elements of the operators defined in the expression (2), for $\alpha = 1$. With equation (17) we determine for each λ an optimized value for α using the condition

$$\frac{\partial E_l}{\partial \alpha} = 0, \quad (18)$$

that together with the expression

$$\mathbf{w}_{ul} \sum_{k=1}^N \left(\alpha^2 \mathbf{K}_{lk} + \alpha \mathbf{V}_{lk}^0 + \frac{1}{\alpha} \mathbf{V}_{lk} \right) \mathbf{w}_{kl} - \mathbf{w}_{sl} \sum_{k=1}^N \left(\alpha^2 \mathbf{K}_{lk} + \alpha \mathbf{V}_{lk}^0 + \frac{1}{\alpha} \mathbf{V}_{lk} \right) \mathbf{w}_{kl} = 0, \quad (19)$$

which corresponds to equation (11), and with

$$\mathbf{w}_{ul} = \sum_{k=1}^N \mathbf{w}_{kl}^2 \quad (20)$$

constitutes, in this case, the MPP algebraic system of nonlinear equations to obtain the variables \mathbf{w}_{kl} and α [20].

2.2. Modified partitioning procedure applied to Zeeman effect

To Zeeman effect we consider a helium-like ion with nuclear charge z . Then, we have

$$\mathbf{H} = \mathbf{H}_0 + \mathbf{V},$$

where \mathbf{H}_0 is in atomic units:

$$\mathbf{H}_0 = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{z}{r_1} - \frac{z}{r_2} \quad (21)$$

with r_i the spatial coordinate of the i th electron. The spherical quadratic Zeeman effect and the electron–electron interaction is represented by additional terms

$$\mathbf{V} = \frac{1}{12} \gamma^2 (r_1^2 + r_2^2) + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (22)$$

The spherical symmetry of this problem leads us to choose the spatial part $|\phi_k\rangle$ of its solution to be expanded in the basis function set

$$\left\{ |\varphi_k\rangle_0 \equiv \left\{ D \frac{1}{2} [1 \pm \mathbf{P}_{12}] \sum_{m_1, m_2} \langle l_1 l_2 m_1 m_2 | LM \rangle |n_1 l_1 m_1\rangle_0 |n_2 l_2 m_2\rangle_0 \right. \right. \\ \left. \left. \text{with } L \text{ and } M \text{ fixed} \right\} \right\}, \quad (23)$$

where D is a normalization factor ($D = 1$ for equivalent electrons and $D = 1/\sqrt{2}$ for the other cases), $L(L+1)$ and M are the eigenvalues of the orbital angular momentum \mathbf{L}^2 and its projection along z -direction L_z , respectively; $\langle l_1 l_2 m_1 m_2 | LM \rangle$ are the Clebsch–Gordan coefficients, \mathbf{P}_{12} is the permutation operator, leading to the interchange of the particles numbered 1 and 2. The kets $|n_i l_i m_i\rangle_0$ ($i = 1, 2$) are one-particle functions obtained from the eigenfunctions $|n_i l_i m_i\rangle$ of the hydrogen-like ions: H, He⁺, Li⁺⁺, etc. after the transformation $z/n_i \rightarrow \alpha$ and a subsequent orthonormalization procedure. The parameter α is introduced in order to optimize the basis set (23). Our calculation is realized for the singlet state ($L = 0$, $M = 0$, S (spin eigenvalue) = 0, parity = positive). Hence, in the set (23) we take $L = 0$, $M = 0$ and the sign $+$. In this case, Zeeman effect, correspondent to equation (17) we have

$$E_l = \sum_{k=1}^N \left(\alpha^2 \mathbf{K}_{lk} + \alpha \mathbf{V}_{lk}^0 + \frac{1}{\alpha^2} \mathbf{V}_{lk} \right) \mathbf{w}_{kl}. \quad (24)$$

For the sake of completeness we calculate and present in tables 7 and 8 the MPP results for the spherical quadratic Zeeman effect in H atom. For this, we have

$$\mathbf{H}_0 = -\frac{1}{2} \nabla^2 - \frac{1}{r} \quad \text{and} \quad \mathbf{V} = \frac{1}{12} \gamma^2 r^2. \quad (25)$$

3. Results and conclusions

3.1. About the Stark effect in the H atom

In tables 1, 2, 4, and 5 we present an analysis of the ground-state energy convergence by increasing the number N of basis functions, for some electric field values. We observe oscillations in the energy values for the spherical Stark effect with $\lambda < 0$ and for the nonspherical Stark effect. This occurs in reason of the potential well with barrier associated to these two problems which also implicates in existence of metastable (quasibound) states. In this case we have taken the lowest value of energy as definite ground-state value because the MPP is a variational method (see the appendix). In all calculations, for the Stark effect, we have used the basis sets $\{|nlm\rangle\}$ and $\{|nlm, \alpha\rangle\}$ with $n = 1, 2, 3, \dots$ and $l = 0$ and $m = 0$ for spherical Stark effect (spherical symmetry) and $l = 0, 1, 2, \dots, n - 1$ and $m = 0$ for nonspherical Stark problem (cylindrical symmetry), since our interest has been the ground state study. We have limited our results to the values of λ for which we have found a larger number results to compare ($0.001 \text{ a.u.} \leq \lambda \leq 0.2 \text{ a.u.}$; $1 \text{ a.u.} = 5.142 \cdot 10^9 \text{ volts/cm}$).

In tables 3 and 6 our results are compared to those obtained by other methods. They show that: (i) with the basis set $\{|nlm\rangle\}$ (noted MPPH) the MPP results, for low values of λ , are comparable to other procedures, but when λ (negative) increases

Table 1

Ground-state energy values ($-E$ in a.u.) for the *spherical Stark effect* in the hydrogen atom for different numbers N of *basis functions* (15) and some field strength values.

$\lambda \setminus N$	3	4	5	10	14	20
-0.002	5.03004	5.03004	5.03004	5.03004	5.03004	5.03004
-0.004	5.06016	5.06017	5.06017	5.06010	5.06019	5.06018
-0.006	5.09037	5.09039	5.09040	5.09041	5.09041	5.09047
-0.01	5.15108	5.15113	5.15116	5.15125	5.15121	5.15121
-0.02	5.30496	5.30370	5.30537	5.30533	5.30533	5.30533
-0.03	5.46327	5.46312	5.46311	5.46311	5.46311	5.46311
-0.04	5.62498	5.62239	5.63331	5.62776	5.62760	5.62753
-0.08	6.48252	6.45843	6.44822	6.43502	6.43284	6.43165
-0.10	7.25651	7.16916	7.13072	7.08026	7.07185	7.06728
0.05	4.2656	4.2666	4.2670	4.2677	4.2678	4.2679
0.10	3.5461	3.5493	3.5509	3.5532	3.5536	3.5538

Table 2

Ground-state energy values ($-E$ in a.u.) for the *nonspherical Stark effect* in the hydrogen atom for different numbers N of *basis functions* (15) and some field strength values.

$\lambda \setminus N$	4	6	10	15	20	24
0.06	5.06783	5.07429	5.07658	5.07761	5.07817	5.07838
0.08	5.14916	5.15757	5.15698	5.15557	5.15465	5.15406
0.10	5.31117	5.31092	5.30963	5.30810	5.30702	5.31093

Table 3

Ground-state energy for the *spherical Stark effect* ($-E$ in a.u.) calculated with our equations, using the standard hydrogen atom wave functions (MPPH) and the optimized basis set (MPP α): comparison with the results of Silva and Canuto (SC) [26], Austin, Killingbeck and Galicia (AKG) [2,15,18] and Killingbeck (K) [16].

λ	SC	SC	AKG	K	MPPH	MPP α
-0.002	0.503006	0.50301			0.503004	0.503006
-0.006	0.509056	0.50906			0.509046	0.509056
-0.010	0.515157	0.51516			0.515121	0.515157
-0.020	0.530664	0.53066	0.530664	0.5307	0.530533	0.530664
-0.030	0.546590	0.54658	0.54659		0.546311	0.546592
-0.040	0.563048	0.56301	0.5631	0.5631	0.563330	0.563067
-0.060	0.598704	0.5979		0.5983	0.598998	0.599334
-0.080	0.639310				0.648252	0.635614
-0.100	0.664333				0.725651	0.677807
0.001	0.498502	0.49850			0.498501	0.498501
0.005	0.492537	0.49254			0.492525	0.492537
0.010	0.485144	0.48514			0.485097	0.485144
0.050	0.428119	0.42807	0.42812	0.4282	0.42679	0.428120
0.070	0.400762	0.4004			0.39809	0.400769
0.100	0.36087		0.36090		0.35537	0.360900
0.150	0.29682		0.29699		0.28468	0.296989

Table 4

Ground-state energy values ($-E$ in a.u.) for the *spherical Stark effect* in the hydrogen atom for different numbers N of *basis functions* (16) and some field strength values.

$\lambda \setminus N$	2	4	6	8	10	14
-0.002	5.03005	5.03006	5.03006	5.03006	5.03006	5.03006
-0.004				5.06024	5.06024	5.06024
-0.006				5.09056	5.09056	5.09056
-0.10	5.15137	5.15157	5.15157	5.15157	5.15157	5.15157
-0.02	5.30569	5.30663	5.30664	5.30664	5.30664	5.30664
-0.03	5.46335	5.46584	5.46591	5.46591	5.46592	5.46592
-0.04	5.62498	5.62239	5.63330	5.62776	5.62760	5.62753
-0.06	5.94171	5.97818	5.99334	5.98943	5.97787	5.96684
-0.08	6.22470	6.34502	6.24474	6.25116	6.35614	6.33477
-0.10	6.77807	6.71199	6.76109	6.58218	6.73954	6.6698
0.05				4.28120	4.28120	4.28120
0.07				4.00769	4.00769	4.00769
0.10				3.60900	3.60900	3.60900
0.15				2.96989	2.96989	2.96989

our results are better, and (ii) with the optimized basis set $\{|nlm, \alpha\rangle\}$ (noted MPP α) our results (table 6) are better than those available in the literature, for all values of λ .

Table 5

Ground-state energy values ($-E$ in a.u.) for the *nonspherical Stark effect* in the hydrogen atom for different numbers N of *basis functions* (16) and some field strength values.

$\lambda \setminus N$	5	10	15	20	25	40
0.05	5.05770	5.05993	5.06089	5.06101	5.06185	5.06113
0.06	5.08402	5.08794	5.09284	5.09408	5.08872	5.08014
0.07	5.11587	5.12610	5.14206		5.13059	5.13072
0.08	5.15362	5.17300	5.07299	5.13521	5.19297	5.17570
0.09	5.19767	5.23222	5.15346	5.19382	5.10444	5.26758
0.10	5.24846	5.30653	5.21714	5.25811	5.19362	5.19853
0.15	5.61349	5.11977	5.65631	5.12856	5.639	5.08440
0.20	6.29867	5.51432	5.25689	5.63013	5.46113	5.69784

Table 6

Ground-state energy for the *nonspherical Stark effect* ($-E$ in a.u.) calculated with our equations, using the standard hydrogen atom wave functions (MPPH) and the optimized basis set (MPP α): comparison with the results of Hehenberger, McIntoch and Brändas (HMB) [13], Farrelly and Reinhardt (FR) [6], Benassi and Grecchi (BG) [3] and Silvestone (S) [28].

λ	HMB	FR	BG	S	MPPH	MPP α
0.05	0.506106	0.506105	0.506105	0.506099	0.505087	0.506341
0.06	0.509203	0.509203	0.509203	0.50918	0.507865	0.509408
0.07	0.513075			0.51294	0.511843	0.514206
0.08	0.517560	0.517561	0.517561	0.5167	0.518001	0.519297
0.09	0.52240			0.5219	0.522807	0.526758
0.10	0.52745	0.527418	0.527418	0.5281	0.531276	0.530653

Table 7

Ground-state energy values ($-E$ in a.u.) for the spherical quadratic Zeeman effect in the hydrogen atom for different numbers N of *basis functions* (16) and some field strength values.

$\gamma \setminus N$	2	4	6	8	10	14
0.1	0.49646	0.49665	0.49752	0.49752	0.49752	0.49752
0.2				0.49032	0.49032	0.49032
0.3				0.47893	0.47893	0.47893
0.5				0.44597	0.44597	0.44597
0.7				0.40264	0.40264	0.40264
1.0		0.30164	0.32378	0.32384	0.32384	0.32384

The application of the MPP to Stark problem confirms its accuracy in the study of the hydrogen atom in the presence of intense electric and magnetic [20] fields (see table 8, column LV).

Table 8

A comparison of the ground-state energy ($-E$ in a.u.) for the H atom calculated with our equations (MPP α), using the optimized standard wave functions (16), with the results of Killingbeck (K) [17], Silva and Canuto (SC1) and (SC2) [27], Brandi (B) [4], Praddaude (P) [24], Le Guillou and Zinn-Justin (LGZJ) [19], Rösner, Wummer, Herold and Ruder (RWHR) [25], Fonte, Falsaperla, Schiffrer and Stanzial (FFSS) [7], Hajj (H) [11], Cabib, Fabri and Fiorio (CFF) [5] and Logrado and Vianna (LV) [20].

γ	MPP α^a	K ^a	SC1 ^a	SC2 ^a	B ^b	P ^b
0.1	0.49752	0.49752	0.49752	0.49752	0.49752	0.49753
0.2	0.49032	0.49032	0.49031	0.49033	0.49026	
0.3	0.47893	0.47893	0.47874	0.47902	0.47850	
0.5	0.44597		0.43918	0.44624	0.44203	
0.7	0.40264			0.40541	0.39332	
1.0	0.32384	0.32384		0.33116	0.27551	0.33117
γ	LGZJ ^b	RWHR ^b	FFSS ^b	H ^b	CFF ^b	LV ^b
0.1		0.497526	0.497526	0.497526	0.49754	0.497526
0.2	0.490382			0.490382	0.49038	0.490382
0.3					0.47920	0.479187
0.5	0.447211				0.44724	0.447211
0.7					0.40571	0.405724
1.0	0.331169	0.331169	0.331169	0.331169	0.33120	0.331169

^a Spherical quadratic Zeeman effect [$H^z = (\gamma^2/12)r^2$].

^b Quadratic Zeeman effect [$H^z = (\gamma^2/8)r^2\sin^2(\theta)$].

3.2. About the Zeeman effect in H, H⁻, He, Li⁺, Be⁺⁺ etc.

For some magnetic field values γ , in table 7 we present the behavior of the MPP results for the H atom when the number N of basis functions is increased. Table 8 presents our results (MPP α) and compares our values to those obtained by several authors. Our results coincide to Killingbeck's values [17], are better than SC1 [27] and comparable to SC2 [27]. The SC2 results, however, were obtained using the factorized wave function approach and perturbation theory; these results, unlike ours, are not variational ones and present oscillations in the energy values when the size of the used expansion is modified. As a consequence, there is not a criterion to choose a conclusive value for E and can occur that E be lower than the ground-state energy. Such a problem does not occur with the MPP results since the MPP method is variational (see the appendix). It is interesting to note, as indicated by Silva and Canuto [27], that the values of E (see table 8) for the spherical quadratic Zeeman effect are a good upper bound for the energy values of the nonspherical quadratic Zeeman effect.

In table 9 and figure 1, we consider the spherical quadratic Zeeman effect for the ion H⁻. Table 9 presents the behavior of the energy values when the number N of basis functions is changed. We note that the MPP method converges monotonically for $\gamma = 0.1$ a.u. but presents oscillations for bigger values. These oscillations are usual for unbound states, also observed in the previous case of the Stark problem;

Table 9
Spherical quadratic Zeeman effect in the H^- ion. Behavior of the ground-state energy ($-E$ in a.u.) with the size N of the basis set (23) for some field strength values γ (a.u.).

$\gamma \setminus N$	10	20	35	56	84	120
0.1	0.509503	0.510944	0.511081	0.511611	0.511635	0.511818
0.2	0.472426	0.475911	0.473614	0.477785	0.477937	0.477363
0.3	0.424719	0.431	0.436	0.432607	0.433	0.42949
0.4	0.371035	0.376553	0.377288	0.376299		
0.5	0.312471	0.319813	0.321072		0.318570	

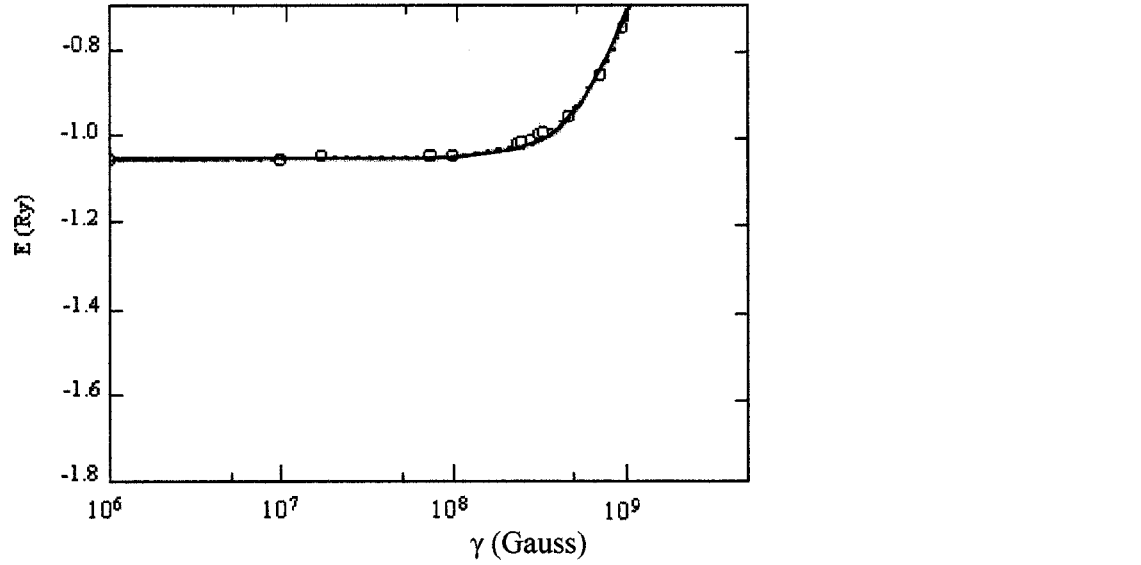


Figure 1. Spherical quadratic Zeeman effect in the H^- ion. The behavior of the ground state energy as a function of the magnetic field γ . —: results of Henry, O'Connell, Smith, Chanmungam and Rajagopal (HOSC) [12] for the quadratic Zeeman effect $H^z = (\gamma^2/8)r^2 \text{sen}^2(\theta)$. -o-: MPP results for the spherical quadratic Zeeman effect $H^z = (\gamma^2/12)r^2$.

in fact, the singlet state ($L = 0$, $M = 0$, $S = 0$, parity = positive) is a bound state for $\gamma \leq 0.05$ a.u. only [12]. In figure 1 our results are compared with the results of Henry et al. [12] obtained for the quadratic Zeeman effect (nonspherical effect) using variational procedure and a basis set composed by Slater's orbitals. Noticing that the ground-state energy for the spherical quadratic Zeeman effect is an upper bound to the nonspherical ground state energy, we can conclude from figure 1 that the ours and Henry et al. [12] results are in good agreement. In tables 10 and 11 we present the results of the spherical quadratic Zeeman effect for helium-like ions ($z = 2, 3, \dots, 6$). An analysis of the behavior of the ground-state energy E as a function of the number N of basis functions shows that the MPP converges monotonically (see table 10, where $\gamma = 0.8$ a.u.) for all ions ($z = 2, 3, \dots, 6$). Our results for ground-state energy considering

Table 10

Spherical quadratic Zeeman effect in the helium-like ions. Analysis of the ground state energies ($-E$ in a.u.) as a function of N (number of basis functions) or $\gamma = 0.8$ a.u. z is the atomic number ($z = 2, 3, \dots, 6$) and γ the magnetic field value.

$z \setminus N$	10	20	35	56	84	120
2	2.77781	2.78427	2.78476	2.78759	2.78774	2.78823
3	7.22413	7.22964	7.23004	7.23144	7.23152	7.23192
4	13.62163	13.62725	13.62766	13.62911	13.62918	13.62958
5	22.00619	22.01198	22.01241	22.01391	22.01400	22.01440
6	32.38610	32.39203	32.39247	32.39402	32.39410	32.39452

Table 11

Spherical quadratic Zeeman effect in the helium-like ions. Energy of the fundamental state ($-E$ in a.u.). γ (a.u.) is the magnetic field and z the atomic number.

$\gamma \setminus z$	2	3	4	5	6
0.1	2.900781	7.277931	13.653795	21.964667	32.351392
0.2	2.894902	7.275710	13.652637	22.028552	32.404074
0.3	2.885246		13.650709	22.027371	32.403277
0.4	2.872000	7.266857	13.648012	22.025718	32.402162
0.5	2.855410	7.260249	13.644547	22.023594	32.400728
0.6	2.835912	7.252210	13.640317	22.020998	32.398975
0.7	2.812349	7.242758	13.635326	22.017932	32.396905
0.8	2.788231	7.231919	13.629576	22.014397	32.394517
1.0	2.726766	7.206181	13.615816	22.005922	32.388788

$0.1 \text{ a.u.} \leq \gamma \leq 1.0 \text{ a.u.}$ are presented in table 11. Comparisons with other methods were not accomplished because we have not found in the literature numerical results for ions with $z \geq 2$. However, as the MPP method has presented very good values for the H and H^- systems in uniform magnetic and electric fields, our MPP results for the He-like ions will be of interest to theoretical and experimental studies of these systems.

Finally we will note that to the field strength values that we have considered the Coulomb interaction is dominating over the magnetic interaction [22]. To more intense field, however, one must use another basis set with a predominantly magnetic character in their spatial factor, as the Landau magnetic wave functions [22], for instance. Works in this direction are in progress and will be published elsewhere. In this context it is interesting to note that the MPP equations are general and can be applied in principle to systems with different forms and (small or large) intensity of the potential \mathbf{V} , in $\mathbf{H} = \mathbf{H}_0 + \mathbf{V}$.

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Appendix

Here, we will show that equations (14) and (17) are equivalent to

$$E_l = \langle \Psi_l | \mathbf{H} | \Psi_l \rangle / \langle \Psi_l | \Psi_l \rangle. \quad (\text{A.1})$$

For this, we substitute equation (13), i.e.,

$$|\Psi_l\rangle = \sum_{k=1}^N \mathbf{w}_{kl} |\varphi_k\rangle \quad (\text{A.2})$$

in expression (A.1), what leads us to

$$E_l = \left(\sum_{s=1}^N \langle \varphi_s | \mathbf{w}_{sl}^* \rangle \mathbf{H} \left(\sum_{k=1}^N \mathbf{w}_{kl} |\varphi_k\rangle \right) \right) / \left\{ \left(\sum_{s=1}^N \langle \varphi_s | \mathbf{w}_{sl}^* \rangle \right) \left(\sum_{k=1}^N \mathbf{w}_{kl} |\varphi_k\rangle \right) \right\}. \quad (\text{A.3})$$

Then, introducing the unit factor $1 = \mathbf{w}_{sl} / \mathbf{w}_{sl}$ at the numerator of equation (A.3) and summing over k in the denominator, we get

$$E_l = \sum_{s=1}^N |\mathbf{w}_{sl}|^2 \left(\sum_{k=1}^N \mathbf{H}_{sk} \mathbf{w}_{kl} / \mathbf{w}_{sl} \right) / \sum_{s=1}^N |\mathbf{w}_{sl}|^2 \quad (\text{A.4})$$

or

$$E_l = \sum_{k=1}^N \mathbf{H}_{lk} \mathbf{w}_{kl} / \mathbf{w}_{ll}, \quad (\text{A.5})$$

where we have used that

$$\mathbf{w}_{ll} = \sum_{s=1}^N |\mathbf{w}_{sl}|^2, \quad (\text{A.6})$$

$$\mathbf{H}_{sk} = \langle \varphi_s | \mathbf{H} | \varphi_k \rangle \quad (\text{A.7})$$

and

$$\sum_{k=1}^N \mathbf{H}_{lk} \mathbf{w}_{kl} / \mathbf{w}_{ll} = \sum_{k=1}^N \mathbf{H}_{sk} \mathbf{w}_{kl} / \mathbf{w}_{sl}. \quad (\text{A.8})$$

We must note that relation (A.8) is reduced to equation (11) when we use

$$\mathbf{H}_{lk} = \mathbf{K}_{lk} + \mathbf{V}_{lk}^0 + \mathbf{V}_{lk} \quad \text{for basis set (15),}$$

and to equation (19) when we use

$$\mathbf{H}_{lk} = \alpha^2 \mathbf{K}_{lk} + \alpha \mathbf{V}_{lk}^0 + \frac{1}{\alpha} \mathbf{V}_{lk} \quad \text{for basis set (16).}$$

Hence, it follows that (A.1) and (A.5) are equivalent equations. Consequently, equations (14) and (17) are equivalent to relation (A.1) and our results satisfy the variation principle with \mathbf{w}_{kl} and α as variational parameters.

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