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Generalized Sturmians applied to atoms in strong external fields

John Avery and Cecilia Coletti

H.C. Ørsted Institute, University of Copenhagen, Denmark

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The generalized Sturmian approach to quantum mechanical many-body problems is described. The method allows correlated solutions to the many-particle Schrödinger equation to be obtained directly, without the use of the self-consistent-field approximation. As an illustrative example, spectra and polarizabilities are calculated for atoms and ions in the 2-electron and 3-electron isoelectronic series under the influence of very strong external electric fields.

1. Introduction

The method of generalized Sturmians [2–19,24–28] offers a fresh approach to the many-particle Schrödinger equation: one avoids the self-consistent-field approximation and obtains directly a correlated solution to the many-particle problem. In this method, one constructs an N-particle basis set whose members are solutions to the Schrödinger equation with a weighted "basis potential", $V_0(\mathbf{x})$:

$$\left[-\sum_{j=1}^{N}\frac{1}{2m_j}\nabla_j^2+\beta_\nu V_0(\mathbf{x})-E\right]\phi_\nu(\mathbf{x})=0, \tag{1}$$

where the weighting factors, β_ν, are chosen in such a way that all the members of the set correspond to the same energy, E. The members of the basis set can then be shown to obey a potential-weighted orthonormality relation in configuration space:

$$\int \mathrm{d}x\ \phi^*_{\nu'}(\mathbf{x})V_0(\mathbf{x})\phi_\nu(\mathbf{x})=\delta_{\nu',\nu}\frac{2E}{\beta_\nu}, \tag{2}$$

while in momentum space, the weighted orthonormality relation becomes

$$\int \mathrm{d}p\ \left(\frac{p_0^2+p^2}{2p_0^2}\right)\phi^{t*}_{\nu'}(\mathbf{p})\phi^t_\nu(\mathbf{p})=\delta_{\nu',\nu}, \tag{3}$$

where

$$p_0^2\equiv -2E. \tag{4}$$

Having constructed such a basis set, we can use it to solve the many-particle Schrödinger equation

$$\left[-\sum_{j=1}^{N} \frac{1}{2m_j} \nabla_j^2 + V(\mathbf{x}) - E \right] \psi(\mathbf{x}) = 0. \tag{5}$$

Expanding $\psi(\mathbf{x})$ in terms of the generalized Sturmian basis, we have

$$\sum_{\nu=1}^{N} \left[-\sum_{j=1}^{N} \frac{1}{2m_j} \nabla_j^2 + V(\mathbf{x}) - E \right] \phi_\nu(\mathbf{x}) B_\nu = 0. \tag{6}$$

Since all the members of the basis set obey equation (1), and since all correspond to the same energy E, we can rewrite (6) in the form

$$\sum_{\nu=1}^{N} \left[-\beta_\nu V_0(\mathbf{x}) + V(\mathbf{x}) \right] \phi_\nu(\mathbf{x}) B_\nu = 0. \tag{7}$$

Multiplying (7) on the left by a conjugate function from our basis set and integrating over the coordinates of the particles in the system, and making use of the potential-weighted orthonormality relation (2), we obtain

$$\sum_{\nu=1}^{N} \left[\int \mathrm{d}x \phi_{\nu'}^*(\mathbf{x}) V(\mathbf{x}) \phi_\nu(\mathbf{x}) - 2E\delta_{\nu',\nu} \right] B_\nu = 0. \tag{8}$$

We now introduce the definition

$$T_{\nu',\nu} \equiv -\frac{1}{p_0} \int \mathrm{d}x \phi_{\nu'}^*(\mathbf{x}) V(\mathbf{x}) \phi_\nu(\mathbf{x}), \tag{9}$$

where p_0 is related to the energy through equation (4). It can be shown that if $V(\mathbf{x})$ represents the potential of a system interacting through Coulomb forces, the matrix $T_{\nu',\nu}$ defined by (9) is independent of p_0. Expressed in terms of this matrix, the generalized Sturmian secular equation becomes

$$\sum_{\nu=1}^{N} [T_{\nu',\nu} - p_0 \delta_{\nu',\nu}] B_\nu = 0. \tag{10}$$

Equation (10) differs from the usual type of secular equation: we are not diagonalizing a Hamiltonian matrix, and we can notice that the kinetic energy term has vanished from (10). Furthermore, the roots are not energies but values of the parameter p_0, which is related to the energy through equation (4).

2. N-electron atoms

We can illustrate the discussion given above by considering the case of an N-electron atom, where the basis potential $V_0(\mathbf{x})$ is chosen to be the nuclear attraction potential

$$V_0(\mathbf{x}) = -\sum_{j=1}^{N} \frac{Z}{r_j}. \tag{11}$$

We now let μ stand for the set of quantum numbers $\{n, l, m, s\}$, and we let $\chi_\mu(\mathbf{x}_j)$ be a hydrogen-like spin-orbital

$$\chi_\mu(\mathbf{x}_j) = R_{nl}(r_j) Y_{lm}(\theta_j, \phi_j) \begin{cases} \alpha(j) \\ \beta(j) \end{cases} \tag{12}$$

with

$$\begin{aligned} R_{nl}(r_j) &= \mathcal{N}_{nl} (2k_\mu r_j)^l \mathrm{e}^{-k_\mu r_j} F(l+1-n \mid 2l+2 \mid 2k_\mu r_j), \\ \mathcal{N}_{nl} &= \frac{2k_\mu^{3/2}}{(2l+1)!} \sqrt{\frac{(l+n)!}{n(n-l-1)!}}. \end{aligned} \tag{13}$$

The functions $\chi_\mu(\mathbf{x}_j)$ are just the familiar hydrogen-like atomic spin-orbitals, except that k_μ has been left as an adjustable parameter instead of being set equal to Z/n. In equation (13), $F(a \mid b \mid z)$ is a confluent hypergeometric function. The functions $\chi_\mu(\mathbf{x}_j)$ defined by (12) and (13) satisfy the relationships

$$\begin{aligned} &\left[-\frac{1}{2}\Delta_j + \frac{1}{2}k_\mu^2 - \frac{nk_\mu}{r_j} \right] \chi_\mu(\mathbf{x}_j) = 0, \\ &\int \mathrm{d}\tau_j \left| \chi_\mu(\mathbf{x}_j) \right|^2 \frac{1}{r_j} = \frac{k_\mu}{n}, \\ &\int \mathrm{d}\tau_j \left| \chi_\mu(\mathbf{x}_j) \right|^2 = 1. \end{aligned} \tag{14}$$

If we construct a Slater determinant based on these functions

$$\phi_\nu(\mathbf{x}) \equiv |\chi_\mu \chi_{\mu'} \chi_{\mu''} \dots| \equiv \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_\mu(\mathbf{x}_1) & \chi_{\mu'}(\mathbf{x}_1) & \chi_{\mu''}(\mathbf{x}_1) & \dots \\ \chi_\mu(\mathbf{x}_2) & \chi_{\mu'}(\mathbf{x}_2) & \chi_{\mu''}(\mathbf{x}_2) & \dots \\ \vdots & \vdots & \vdots & \vdots \\ \chi_\mu(\mathbf{x}_N) & \chi_{\mu'}(\mathbf{x}_N) & \chi_{\mu''}(\mathbf{x}_N) & \dots \end{vmatrix} \tag{15}$$

and if we impose the subsidiary conditions

$$\begin{aligned} &k_\mu^2 + k_{\mu'}^2 + k_{\mu''}^2 + \dots = -2E \equiv p_0^2, \\ &nk_\mu = n'k_{\mu'} = n''k_{\mu''} = \dots = Z\beta_\nu \equiv Q_\nu, \end{aligned} \tag{16}$$

then $\phi_\nu(\mathbf{x})$ will satisfy equation (1). This follows from (14) because

$$\left[-\sum_{j=1}^{N}\frac{1}{2}\nabla_j^2\right]\phi_\nu(\mathbf{x}) = \left[\frac{1}{2}k_\mu^2 - \frac{nk_\mu}{r_1} + \frac{1}{2}k_{\mu'}^2 - \frac{n'k_{\mu'}}{r_2} + \cdots\right]\phi_\nu(\mathbf{x})$$
$$= \left[-E - \frac{\beta_\nu Z}{r_1} - \frac{\beta_\nu Z}{r_2} - \cdots\right]\phi_\nu(\mathbf{x})$$
$$= \left[-E + \beta_\nu V_0(\mathbf{x})\right]\phi_\nu(\mathbf{x}). \tag{17}$$

It can also be shown [5–8,13] that, as a consequence of (14) and (16), the functions $\phi_\nu(\mathbf{x})$ are automatically normalized in accordance with equation (2). It can be seen that the generalized Sturmian method applied to atoms is a form of configuration interaction, but with a special prescription for the construction of optimal configurations. Each configuration is characterized by a set of one-electron quantum numbers, $\nu = \{\mu, \mu', \mu'', \ldots\}$, and by an effective nuclear charge, $Q_\nu = \beta_\nu Z$. The effective charge is chosen by means of the subsidiary conditions (16) in such a way that all the configurations are solutions to equation (1), and all correspond to the same value of E. From the subsidiary conditions (16) it follows that

$$\frac{k_\mu}{p_0} = \frac{1}{n\sqrt{\dfrac{1}{n^2} + \dfrac{1}{n'^2} + \dfrac{1}{n''^2} + \cdots}} \tag{18}$$

and that

$$-\frac{1}{p_0}\int \mathrm{d}x\ \phi_{\nu'}^*(\mathbf{x})V_0(\mathbf{x})\phi_\nu(\mathbf{x}) = Z\delta_{\nu',\nu}\sqrt{\frac{1}{n^2} + \frac{1}{n'^2} + \frac{1}{n''^2} + \cdots}, \tag{19}$$

the sums in (18) and (19) being taken over all the principal quantum numbers in the configuration ν.

3. Atoms in strong external fields

The generalized Sturmian method is especially well suited to calculations of the effect of external fields on atoms, when the fields are so strong that perturbation theory must fail. The Sturmian secular equation then takes on the form

$$\sum_\nu \left[Z\delta_{\nu',\nu}\sqrt{\frac{1}{n^2} + \frac{1}{n'^2} + \cdots} + T'_{\nu',\nu} + T''_{\nu',\nu} - p_0\delta_{\nu',\nu}\right]B_\nu = 0, \tag{20}$$

where

$$T'_{\nu',\nu} = -\frac{1}{p_0}\int \mathrm{d}x\ \phi_{\nu'}^*(\mathbf{x})\sum_{i>j}^{N}\sum_{j=1}^{N}\frac{1}{r_{ij}}\phi_\nu(\mathbf{x}) \tag{21}$$

is the interelectron repulsion matrix, while $T''_{\nu',\nu}$ represents the contribution of the external field. For example, if an atom is subjected to an external electric field of strength $\mathcal{E}$ in the direction of the z axis, then

$$T''_{\nu',\nu} = -\eta M_{\nu',\nu}, \tag{22}$$

where

$$\eta \equiv \frac{\mathcal{E}}{p_0^2} \tag{23}$$

and

$$M_{\nu',\nu} \equiv \int \mathrm{d}x\ \phi^*_{\nu'}(\mathbf{x}) \sum_{j=1}^{N} p_0 z_j \phi_\nu(\mathbf{x}). \tag{24}$$

When a generalized Sturmian basis set of the form shown in (15) is used, and when the subsidiary conditions (16) are imposed, then both $T'_{\nu',\nu}$ and $M_{\nu',\nu}$ turn out to be composed of numbers which are independent of p_0. Thus we can proceed in the following manner. Having evaluated $T'_{\nu',\nu}$ and $M_{\nu',\nu}$, we pick a value of η and a value of Z. This gives us a spectrum of p_0 values; and (23) may then be used to find the value of $\mathcal{E}$ corresponding to each root. The diagonalization can then be repeated for other values of η, and by interpolation, curves representing $p_0(\mathcal{E})$ and $E(\mathcal{E})$ can be constructed for the ground state of the atom and for the excited states. The induced dipole moment of the ground state can also be calculated as a function of the field strength $\mathcal{E}$. Finally, the whole calculation can be repeated for other values of Z. The heavy computational step in this procedure is not the repeated solution of the secular equation, since this involves only the diagonalization of a matrix of moderate size. The heavy step is the original calculation of $T'_{\nu',\nu}$ and $M_{\nu',\nu}$. In the construction of these matrices, the generalized Slater–Condon rules [1,20–23] must be used. When we take the matrix element of an operator between two configurations, we must remember that they may be characterized by different values of the effective charge, Q_ν. Thus, radial orthogonality cannot always be assumed between atomic orbitals belonging to different configurations. However, $T'_{\nu',\nu}$ and $M_{\nu',\nu}$ need never be recalculated; and once constructed, these two matrices give us the behavior of the entire N-electron isoelectronic series of atoms and ions for all values of the external field strength.

4. The 2-electron isoelectronic series and the 3-electron isoelectronic series

As an illustration of the methods discussed above we have applied them to calculations on the 2-electron isoelectronic series, He, Li^+, Be^{2+}, B^{3+}, C^{4+}, ..., and on the 3-electron series, Li, Be^+, B^{2+}, C^{3+}, ..., subjected to external electric fields so strong that perturbation theory could not be used.

If a strong external electric field is applied to an atom, a dipole moment is induced in the ground state, and the spectrum of the excited states is altered. Finally, when

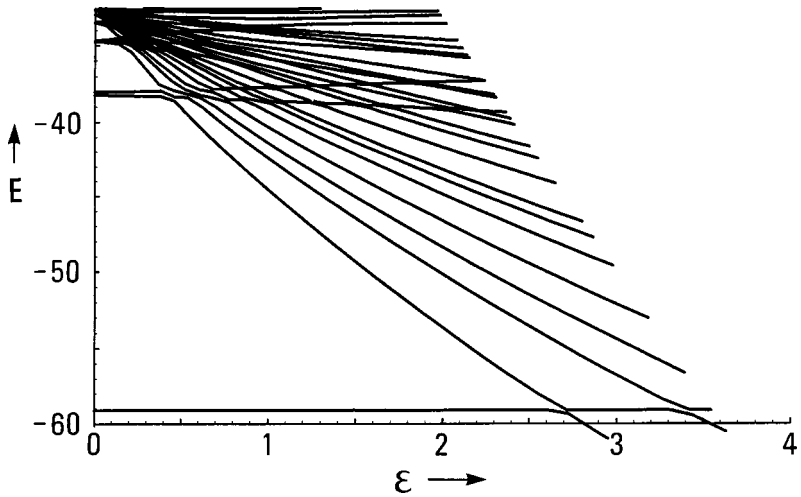

Figure 1. This figure shows the spectrum of the ion O^{6+} as a function of the applied field. Only the states with $M = 0$ are shown. Atomic units are used in this figure, that is to say the energy of the states of the ion are measured in Hartrees, while the applied field is measured in Hartrees/electron-Bohr. As can be seen in the figure an avoided crossing between the first excited state and the ground state occurs when the applied field is 2.7 Hartrees/electron-Bohr. Until this value of the applied field, the polarizability of the ground state is very nearly constant, but when the avoided crossing occurs the polarizability increases sharply, and tunneling into the external potential well produced by the field becomes possible (the preionization anomaly).

the field becomes sufficiently strong, electron tunneling can occur from the attractive potential well of the nucleus into the large exterior potential well produced by the field. Thus, a sufficiently strong external field can produce spontaneous ionization; and as the ionization limit is approached, anomalies occur not only in the spectrum of the atom or ion, but also in the polarizability and in the character of the ground state. For the 2-electron isolectronic series, the induced polarization of the ground state increases very nearly linearly with increasing field until the preionization anomaly occurs. In other words, the polarizability of the 2-electron series is approximately constant up to the point of the preionization anomaly. At that point, there is a sudden onset of increasingly high polarizability, followed by ionization. The point at which the anomaly occurs corresponds to an avoided crossing between the ground state and the first excited state, as illustrated in figure 1, which was the result of a calculation using 45 configurations. It can be seen from the figure that avoided crossings of excited states occur at considerably lower values of the applied field and thus when the first excited state makes its avoided crossing with the ground state it already contains components corresponding to high values of angular momentum. These give the post-crossing ground state its suddenly increased polarizability. The new ground state is almost able to tunnel into the external potential well.

The behavior of the 3-electron isoelectronic series is qualitatively different. Instead of being essentially constant up to the preionization anomaly, the polarizability

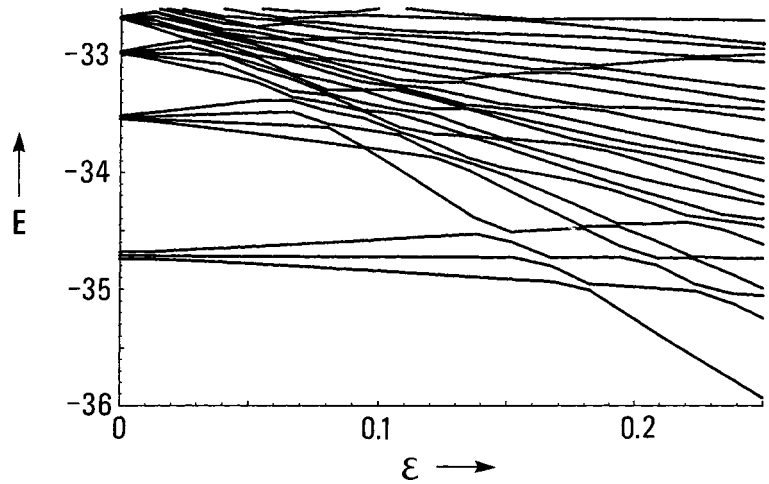

Figure 2. This figure again shows the spectrum of O^{6+} as a function of the applied field. The figure shows in detail the part of the spectrum shown in the upper left-hand corner of figure 1.

Table 1
Low-field polarizabilities of atoms and ions in the 2-electron and 3-electron isoelectronic series. The polarizabilities are expressed in atomic units, i.e. (electron-Bohr)^2/Hartree = (Bohr)^3.

Z	$N = 2$	$N = 3$
2	1.582011	
3	0.198317	182.77610
4	0.051370	28.99684
5	0.018780	8.69635
6	0.008415	3.65967
7	0.004314	1.86972
8	0.002435	0.94998

of the 3-electron series first is large. The polarizability (i.e. the slope of the curve showing induced dipole moment as a function of field strength) then diminishes for intermediate values of field and finally increases sharply at the preionization anomaly. This qualitative difference in behavior can be understood by considering the large energy gap between the ground state in the 2-electron series and the first excited states. By contrast, the 3-electron series has available a $2P$ state near in energy to the ground state which readily hybridizes with the ground state under the influence of the external field. The availability of this $2P$ state accounts for the much larger initial polarizability of the 3-electron isoelectronic series which can be seen in table 1. However, once the nearby $2P$ state has been fully utilized, the system has no other nearby states of higher angular momentum and thus the polarizability falls before increasing again at the preionization anomaly. Figure 3 shows the induced dipole moment of O^{5+} as a function of the external field. The line marked (a) in the figure shows the induced

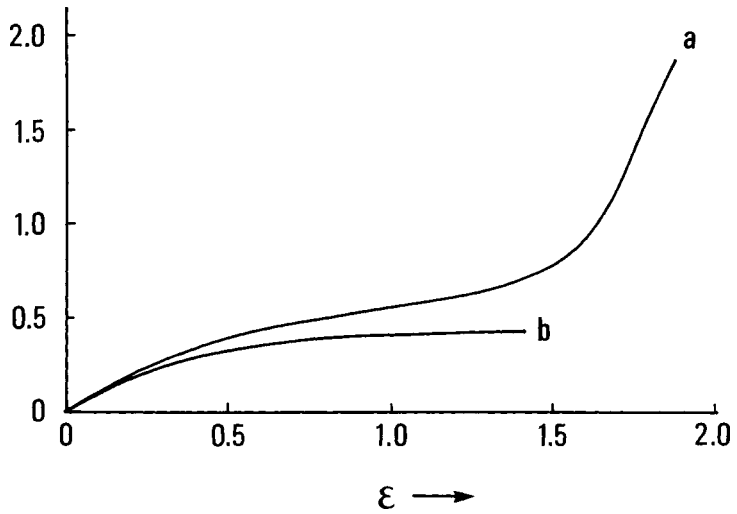

Figure 3. The curve marked (a) shows the induced dipole moment of O^{5+} as a function of the external field. The polarizability of this 3-electron ion corresponds to the slope of the curve. Curve (a) was calculated using 9 configurations, while for comparison curve (b) was calculated using only the configurations $|\chi_{1s}\chi_{\overline{1s}}\chi_{2s}|$ and $|\chi_{1s}\chi_{\overline{1s}}\chi_{2p_0}|$. It can be seen from the figure that the initial polarizability is due almost entirely to hybridization between these two configurations, which lie close together in energy. At an applied field of 1.6 Hartrees/electron-Bohr a preionization anomaly occurs and the polarizability increases sharply. This anomaly corresponds in the spectrum to an avoided crossing between the ground state and the first excited state.

dipole moment calculated with nine configurations, while the line marked (b) was calculated using only the configuration $|\chi_{1s}\chi_{\bar{1}s}\chi_{2s}|$ and the configuration $|\chi_{1s}\chi_{\bar{1}s}\chi_{2p_0}|$. It can be seen from the figure that the initial polarizability is due almost entirely to the nearby $2P$ configuration.

In a future publication, we hope to use similar methods to study the behavior of atoms and ions in very strong magnetic fields, and we hope also to be able to extend the formalism to the study of time-dependent phenomena.

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