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The generalized Sturmian method for calculating spectra of atoms and ions

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The properties of generalized Sturmian basis sets are reviewed, and functions of this type are used to perform direct configuration interaction calculations on the spectra of atoms and ions. Singlet excited states calculated in this way show good agreement with experimentally measured spectra. When the generalized Sturmian method is applied to atoms, the configurations are constructed from hydrogenlike atomic orbitals with an effective charge which is characteristic of the configuration. Thus, orthonormality between the orbitals of different configurations cannot be assumed, and the generalized Slater–Condon rules must be used. This aspect of the problem is discussed in detail. Finally spectra are calculated in the presence of a strong external electric field. In addition to the expected Stark effect, the calculated spectra exhibit anomalous states. These are shown to be states where one of the electrons is primarily outside the atom or ion, with only a small amplitude inside.

0. Introduction

When exact solutions to the Schrödinger equation for hydrogenlike atoms became available in the late 1920s, it was at first thought that sets of these functions could be used as basis sets for building up the wave functions of many-electron atoms and molecules. However, it was soon realized that hydrogenlike orbitals do not form a complete set unless the continuum is included, with all the attendant difficulties. To overcome this problem, Shull and Löwdin [1] introduced one-electron radial basis sets where a constant exponential factor e^{-kr} was multiplied by an infinite set of linearly independent polynomials in r, and these authors were able to show that a basis of this type is complete in the sense that all well behaved functions of r obeying the same boundary conditions can be exactly represented in terms of them. Later Rotenberg [2,3] gave the name "Sturmian" to basis functions of this type, because he wished to emphasize their connection with Sturm–Liouville theory. The work of Fock, Shibuya, Wulfman, Aquilanti and others [4–12] has established the connection between Fourier-transformed Sturmian basis functions and the theory of hyperspherical harmonics [13–16]. Weniger [17] has pointed

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out that the potential-weighted orthonormality relations of Sturmian basis sets indicate that they span a function space of the Sobolev type.

In 1968, Goscinski [18] completed an important study in which he generalized the concept of Sturmian basis sets. He regarded Sturmians as solutions to the Schrödinger equation with a weighted zeroth-order potential, each solution having its own weighting factor, chosen in such a way as to make all the solutions correspond to the same value of the energy regardless of their quantum numbers. Generalized Sturmian basis sets of the Goscinski type can be used to perform direct configuration interaction calculations both on atoms and on molecules [19–30]. In the present paper, we shall begin by discussing the properties of one-electron hydrogenlike Sturmian basis sets. We will next discuss generalized Sturmians. Finally we will apply generalized Sturmians to the calculation of the spectra of atoms and ions, and the effects of a strong external electric field will also be considered.

1. One-electron hydrogenlike Sturmians

We can define a one-electron hydrogenlike Sturmian basis set by the relations

$$\chi_{nlm}(\mathbf{x}) = R_{nl}(r)Y_{lm}(\theta,\phi), \tag{1}$$

where $Y_{lm}(\theta,\phi)$ is a spherical harmonic, and where the radial function is given by

$$R_{nl}(r) = \mathcal{N}_{nl}(2kr)^l\,\mathrm{e}^{-kr}F(l+1-n\mid 2l+2\mid 2kr) \tag{2}$$

with the normalizing factor

$$\mathcal{N}_{nl} = \frac{2k^{3/2}}{(2l+1)!}\sqrt{\frac{(l+n)!}{n(n-l-1)!}}. \tag{3}$$

The function F which appears in equation (2) is a confluent hypergeometric function:

$$F(a|b|x) = 1 + \frac{ax}{b} + \frac{a(a+1)x^2}{b(b+1)2!} + \cdots. \tag{4}$$

If k is set equal to Z/n, these correspond to the familiar hydrogenlike radial functions. On the other hand, when k is held constant, the one-electron basis set defined by equations (1)–(4) correspond to the Sturmian basis functions introduced by Shull and Löwdin, who were able to show that such a basis set is complete without the inclusion of the continuum. One might ask why completeness is so important, since in practice one always truncates a basis set. The answer is that the usual hydrogenlike radial functions, which are polynomials multiplied by $\mathrm{e}^{-Zr/n}$, have nodes at increasingly large values of r as n increases. Thus, the radial functions corresponding to large values of n are not very useful for constructing an approximate series representation of a function whose nodes occur at small values of r. Calculational experience has shown that a series of Sturmians is able to give a very accurate and rapidly convergent representation of an atomic or molecular orbital, and therefore, Sturmian basis sets are becoming more and more widely used in the quantum mechanical treatment of many-electron systems. The Shull–Löwdin Sturmians are solutions of the differential equation

$$\left[-\frac{1}{2}\nabla^2 + \frac{1}{2}k^2 - \frac{nk}{r}\right]\chi_{nlm}(\mathbf{x}) = 0. \tag{5}$$

Notice that if k were replaced by Z/n, this would be the differential equation obeyed by the familiar hydrogenlike orbitals; but for the Sturmians, the energy $-k^2/2$ is the same for all the members of the basis set, regardless of the quantum numbers. Another (complex conjugated) member of the basis set, with quantum numbers n', l', and m', will obey

$$\left[-\frac{1}{2}\nabla^2 + \frac{1}{2}k^2 - \frac{n'k}{r}\right]\chi^*_{n'l'm'}(\mathbf{x}) = 0. \tag{6}$$

We can use equations (5) and (6) to show that the Sturmians obey a potential-weighted orthogonality relation in direct space: if we multiply the equations from the left respectively by $\chi^*_{n'l'm'}(\mathbf{x})$ and $\chi_{nlm}(\mathbf{x})$, and if we afterwards integrate over coordinates and take the difference between the two equations, making use of Hermiticity, we obtain

$$(n - n')\int d^3x\,\chi^*_{n'l'm'}(\mathbf{x})\frac{1}{r}\chi_{nlm}(\mathbf{x}) = 0. \tag{7}$$

Therefore, the potential-weighted integral in equation (7) must vanish if $n \neq n'$; and from the orthogonality of the spherical harmonics, we know that the integral must also vanish if $l \neq l'$ and/or $m \neq m'$. With the normalization shown in equation (3), the potential-weighted orthonormality relation obeyed by the Sturmian basis set is

$$\int \mathrm{d}^3x\;\chi^*_{n'l'm'}(\mathbf{x})\frac{1}{r}\chi_{nlm}(\mathbf{x}) = \frac{k}{n}\delta_{n'n}\delta_{l'l}\delta_{m'm}. \tag{8}$$

One can use a basis set of this type to solve the time-independent Schrödinger equation for an electron moving in an arbitrary potential $V(\mathbf{x})$, but for rapid convergence, $V(\mathbf{x})$ should have some resemblance to the "zeroth-order" potential, $V_0(\mathbf{x}) = -Z/r$. Calculational experience shows that convergence is most rapid if the condition $E = -k^2/2$ is imposed. In other words, it is desirable to set the parameter k, which governs the exponential decay of all the functions in the Sturmian basis set, equal to $\sqrt{-2E}$, where E is the energy of the eigenfunction being expanded. This could be done iteratively, starting with a guessed value of k, solving the secular equations for the state of interest, thus determining E, and repeating the calculation with a $k = \sqrt{-2E}$ to obtain an improved value of E, and so on. An alternative and much more efficient method for imposing the condition linking k to E will be discussed below in connection with generalized Sturmians.

2. Generalized Sturmians

We can define a generalized Sturmian basis set of the Goscinski type as a set of solutions of the Schrödinger equation

$$\left[-\frac{1}{2}\Delta + \beta_\nu V_0(\mathbf{x}) - E\right]\phi_\nu(\mathbf{x}) = 0, \tag{9}$$

where Δ is the Laplacian operator, $V_0(\mathbf{x})$ is a zeroth-order potential, and where the constants β_ν are chosen in such a way that all of the solutions to equation (9) correspond to the same value of the energy E, regardless of their quantum numbers ν. The one-electron hydrogenlike Sturmians discussed in equations (1)–(8) are special cases of solutions to (9) with $V_0(\mathbf{x}) = -Z/r$ and $\beta_\nu = nk/Z$: all the functions in the basis set correspond to the same value of k and hence to the same value of $E = -k^2/2$. By an argument similar to that given in equations (5)–(8), one can show that the set of isoenergetic solutions to (9) obeys potential-weighted orthonormality relations analogous to (8):

$$\int \mathrm{d}x\, \phi^*_{\nu'}(\mathbf{x}) V_0(\mathbf{x})\phi_\nu(\mathbf{x}) = \delta_{\nu',\nu}\frac{2E}{\beta_\nu}, \tag{10}$$

where the normalization has been chosen in such a way that the orthonormality relations (10) reduce to (8) for one-electron hydrogenlike Sturmians. However, it is only when $\beta_{\nu'} \neq \beta_\nu$ that the potential-weighted orthogonality of (10) follows automatically. In cases where $\beta_{\nu'} = \beta_\nu$ and $\nu' \neq \nu$ it must be either established using symmetry arguments or else especially constructed.

Goscinski's way of looking at Sturmians makes generalization very easy. For example, we can let (9) be the Schrödinger equation of an N-electron system, so that

$$\mathbf{x} = \{\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N\}, \tag{11}$$

where

$$\mathbf{x}_j \equiv \{x_j, y_j, z_j\}, \quad j = 1, 2, \ldots, N. \tag{12}$$

In that case, the operator Δ is the generalized Laplacian operator

$$\Delta \equiv \sum_{j=1}^{N} \nabla_j^2. \tag{13}$$

In the generalized Sturmian method, just as in perturbation theory, many choices of the zeroth-order potential $V_0(\mathbf{x})$ are possible; but it is desirable to choose $V_0(\mathbf{x})$ to be as close as possible to the actual potential $V(\mathbf{x})$ for which solutions to the many-electron Schrödinger equation are desired. If the zeroth-order potential is taken to be a sum of one-electron potentials, so that

$$V_0(\mathbf{x}) = \sum_{j=1}^{N} v(\mathbf{x}_j), \tag{14}$$

then the N-electron Schrödinger equation (9) is separable into one-electron equations. Various choices of the zeroth-order one-electron potential $v(\mathbf{x}_j)$ are possible. For example, in atomic calculations, one might use the Kohn–Sham potential. In the present paper, we will let $v(\mathbf{x}_j)$ be the nuclear attraction potential experienced by the jth electron in an atom, so that

$$V_0(\mathbf{x}) = -\sum_{j=1}^{N} \frac{Z}{r_j}. \tag{15}$$

Then equation (9) has exact solutions of the form

$$\phi_\nu(\mathbf{x}) = |\chi_{n,l,m,m_s}\chi_{n',l',m',m'_s}\chi_{n'',l'',m'',m''_s}\cdots|. \tag{16}$$

The spin-orbitals which appear in the Slater determinant shown in equation (16) are just the familiar solutions to the Schrödinger equation for an electron moving in the field of a bare nucleus with effective charge Q_ν, where

$$Q_\nu = \beta_\nu Z = \left(\frac{-2E}{1/n^2 + 1/n'^2 + \cdots}\right)^{1/2}. \tag{17}$$

In other words, each configuration ϕ_ν is characterized by an effective charge Q_ν, and it is a Slater determinant built of hydrogenlike atomic spin-orbitals of the form shown in equations (1)–(4) and table 1, with k replaced by Q_ν/n. The one-electron hydrogenlike spin-orbitals which are used to build up the configuration $\phi_\nu(\mathbf{x})$ are solutions of the differential equation

$$\left[-\frac{1}{2}\nabla_j^2 + \frac{Q_\nu^2}{2n^2} - \frac{Q_\nu}{r_j}\right]\chi_{n,l,m,m_s}(\mathbf{x}_j) = 0, \tag{18}$$

and therefore, making use of equations (13) and (15)–(17), we have

$$\begin{aligned}\left[-\frac{1}{2}\Delta\right]\phi_\nu(\mathbf{x}) &= \left[-\frac{Q_\nu^2}{2}\left(\frac{1}{n^2} + \frac{1}{n'^2} + \cdots\right) + \frac{Q_\nu}{r_1} + \frac{Q_\nu}{r_2} + \cdots\right]\phi_\nu(\mathbf{x}) \\ &= \left[E - \beta_\nu V_0(\mathbf{x})\right]\phi_\nu(\mathbf{x}).\end{aligned} \tag{19}$$

Therefore, configurations of the form indicated in equations (16) and (17) are solutions to the zeroth-order many-electron Schrödinger equation (9).

3. Calculation of atomic spectra using generalized Sturmians

It is convenient to introduce the definitions:

$$p_0 \equiv \sqrt{-2E} \tag{20}$$

and

$$\mathcal{R} \equiv \sqrt{\frac{1}{n^2} + \frac{1}{n'^2} + \cdots}. \tag{21}$$

Table 1

The first few hydrogenlike radial Sturmians generated by equations (2)–(4). If one replaces k by Z/n, these functions correspond to the familiar hydrogenlike radial functions, which do not form a complete set unless the continuum is included. However, when k is held constant, the set is complete.

$$\begin{aligned}
R_{1,0}(r) &= 2k^{3/2}\,\mathrm{e}^{-kr}\\
R_{2,0}(r) &= 2k^{3/2}(1-kr)\,\mathrm{e}^{-kr}\\
R_{2,1}(r) &= \frac{2k^{5/2}}{\sqrt{3}}r\,\mathrm{e}^{-kr}\\
R_{3,0}(r) &= 2k^{3/2}\left(1-2kr+\frac{2k^2r^2}{3}\right)\mathrm{e}^{-kr}\\
R_{3,1}(r) &= \frac{(2k)^{5/2}}{3}r\left(1-\frac{kr}{2}\right)\mathrm{e}^{-kr}\\
R_{3,2}(r) &= \frac{2^{3/2}k^{7/2}}{3\sqrt{5}}r^2\,\mathrm{e}^{-kr}\\
R_{4,0}(r) &= 2k^{3/2}\left(1-3kr+2k^2r^2-\frac{k^3r^3}{3}\right)\mathrm{e}^{-kr}\\
R_{4,1}(r) &= 2\sqrt{\frac{5}{3}}k^{5/2}r\left(1-kr+\frac{k^2r^2}{5}\right)\mathrm{e}^{-kr}\\
R_{4,2}(r) &= \frac{2k^{7/2}}{\sqrt{5}}r^2\left(1-\frac{kr}{3}\right)\mathrm{e}^{-kr}\\
R_{4,3}(r) &= \frac{2k^{9/2}}{3\sqrt{35}}r^3\,\mathrm{e}^{-kr}
\end{aligned}$$

With these definitions, equation (17) can be written in the form

$$Q_\nu = \beta_\nu Z = \frac{p_0}{\mathcal{R}}, \tag{22}$$

while the energy of the N-electron system becomes

$$E = -\frac{p_0^2}{2}. \tag{23}$$

The non-relativistic Schrödinger equation for an N-electron atom has the form

$$\left[-\frac{1}{2}\Delta + V(\mathbf{x}) - E\right]\psi(\mathbf{x}) = 0, \tag{24}$$

where

$$V(\mathbf{x}) = V_0(\mathbf{x}) + V'(\mathbf{x}) = -\sum_{j=1}^{N}\frac{Z}{r_j} + \sum_{i>i}^{N}\sum_{i=1}^{N}\frac{1}{r_{ij}}. \tag{25}$$

In equation (25), V_0 is the nuclear attraction term, while V' represents the effects of interelectron repulsion. If we introduce the definition

$$T^0_{\nu',\nu} \equiv -\frac{1}{p_0}\int \mathrm{d}x\, \phi^*_{\nu'}(\mathbf{x})V_0(\mathbf{x})\phi_\nu(\mathbf{x}), \tag{26}$$

then it follows from equations (10), (22) and (23) that

$$T^0_{\nu',\nu} = \delta_{\nu'\nu}Z\mathcal{R}. \tag{27}$$

It is interesting to notice that the matrix $T^0_{\nu',\nu}$ of equations (26) and (27) is independent of p_0, and thus, independent of the energy E. It can similarly be shown that the matrix

$$T'_{\nu',\nu} \equiv -\frac{1}{p_0}\int \mathrm{d}x\, \phi^*_{\nu'}(\mathbf{x})V'(\mathbf{x})\phi_\nu(\mathbf{x}) \tag{28}$$

is also independent of p_0. We are now in a position to write down the Sturmian secular equation for an N-electron atom. If we expand the wave function in terms of the generalized Sturmian basis set $\phi_\nu(\mathbf{x})$,

$$\psi(\mathbf{x}) = \sum_\nu \phi_\nu(\mathbf{x})B_\nu, \tag{29}$$

then the Schrödinger equation (24) becomes

$$\sum_\nu \left[-\frac{1}{2}\Delta + V(\mathbf{x}) - E\right]\phi_\nu(\mathbf{x})B_\nu = 0. \tag{30}$$

Making use of equation (19), we can rewrite (30) in the form:

$$\sum_\nu \left[V(\mathbf{x}) - \beta_\nu V(\mathbf{x})\right]\phi_\nu(\mathbf{x})B_\nu = 0. \tag{31}$$

We now multiply on the left by $\phi^*_{\nu'}(\mathbf{x})$ and integrate over the coordinates:

$$\sum_\nu \int \mathrm{d}x\, \phi^*_{\nu'}(\mathbf{x})\left[V(\mathbf{x}) - \beta_\nu V(\mathbf{x})\right]\phi_\nu(\mathbf{x})B_\nu = 0. \tag{32}$$

If we next make use of equations (10), (21), and (25)–(28) and divide by p_0, we can rewrite (32) in the form:

$$\sum_\nu \left[\delta_{\nu',\nu}Z\mathcal{R} + T'_{\nu',\nu} - p_0\delta_{\nu',\nu}\right]B_\nu = 0, \tag{33}$$

where the interelectron repulsion matrix $T'_{\nu',\nu}$ is independent of p_0. Equation (33) is the generalized Sturmian secular equation for an N-electron atom or ion, and it has several interesting features:

1. The kinetic energy term has disappeared.
2. The eigenvalues are not energies, but values of the parameter p_0, which is related to the energy by equations (20) and (23).

Table 2

^1S excited state energies (in hartrees) for the two-electron isoelectronic series. In tables 2–5, the basis set used consisted of generalized Sturmians of the Goscinski type. Experimental values are taken from the NIST tables (`http://physics.nist.gov/asd`). Some of the discrepancy between calculated and experimental energies for the ions with higher Z may be due to experimental inaccuracies, since, for an isoelectronic series, the accuracy of the generalized Sturmian method increases with increasing atomic number. The calculations were done on a 499 MHz Intel Pentium III. Both ^3S (not shown here) and ^1S states were done simultaneously using a basis of 63 functions, spending in all about 0.5 s for the 154 calculated states. ^1P and ^1D excited states were each calculated using 40 basis functions, each table requiring less than 0.2 s of CPU time.

	He	Li^+	Be^{2+}	B^{3+}	C^{4+}	N^{5+}	O^{6+}
$1s^2\ ^1S$	−2.8911	−7.2656	−13.640	−22.015	−32.390	−44.765	−59.140
expt.	−2.9033	−7.2798	−13.656	−22.034	−32.415	−44.801	−59.192
$1s2s\ ^1S$	−2.1429	−5.0331	−9.1735	−14.564	−21.206	−29.098	−38.241
expt.	−2.1457	−5.0409	−9.1859	−14.582	−21.229	−29.131	−38.286
$1s3s\ ^1S$	−2.0603	−4.7297	−8.5100	−13.402	−19.406	−26.521	−34.748
expt.	−2.0610	−4.7338	−8.5183	−13.415	−19.231	−26.547	−34.786
$1s4s\ ^1S$	−2.0331	−4.6275	−8.2837	−13.002	−18.784	−25.629	−33.537
expt.	−2.0333	−4.6298	−8.2891	−13.029	−18.821	−25.653	−33.571
$1s5s\ ^1S$	−2.0209	−4.5811	−8.1805	−12.819	−18.499	−25.219	−32.979
expt.	−2.0209	−4.5825	−8.1905		−18.523	−25.241	−33.026
$1s6s\ ^1S$	−2.0144	−4.5561	−8.1249	−12.721	−18.345	−24.997	−32.678
expt.	−2.0143	−4.5570			−18.363		
$1s7s\ ^1S$	−2.0105	−4.5411	−8.0916	−12.662	−18.253	−24.864	−32.496
expt.	−2.0104	−4.5417			−18.268		
$1s8s\ ^1S$	−2.0080	−4.5314	−8.0701	−12.624	−18.193	−24.778	−32.379
expt.	−2.0079	−4.5328			−18.206		
$1s9s\ ^1S$	−2.0063	−4.5248	−8.0554	−12.597	−18.152	−24.719	−32.299
expt.	−2.0061						
$1s10s\ ^1S$	−2.0047	−4.5201	−8.0448	−12.579	−18.123	−24.677	−32.241
expt.	−2.0049						
$1s11s\ ^1S$	−2.0011	−4.5163	−8.0370	−12.565	−18.102	−24.646	−32.199
expt.	−2.0040						

3. The basis set is not completely determined until after the secular equation has been solved. Only the form of the basis set is known, but not the “scaling factor”, p_0.
4. Solving the secular equation yields a spectrum of p_0 values, and thus, through equation (23), a spectrum of energies. For each energy, the basis set is different, since each has its own value of p_0. The basis sets which are appropriate for the excited states correspond to low values of p_0, and they are thus more diffuse than the basis set used to represent the ground state.

Table 2 shows some ^1S excited states of the two-electron isoelectronic series of atoms and ions, calculated by solving equation (33) with generalized Sturmian basis functions. The interelectron repulsion matrix $T'_{\nu',\nu}$ was calculated only once, and then (33) was solved several times, using the same interelectron repulsion matrix for various values of the nuclear charge Z.

Table 3

^1P excited state energies for the two-electron isoelectronic series.

	He	Li^+	Be^{2+}	B^{3+}	C^{4+}	N^{5+}	O^{6+}
$1s2p\ ^1P$	−2.1218	−4.9950	−9.1217	−14.500	−21.130	−29.011	−38.142
expt.	−2.1236	−4.9934	−9.1117	−14.480	−21.100	−28.974	−38.100
$1s3p\ ^1P$	−2.0546	−4.7201	−8.4971	−13.385	−19.386	−26.498	−34.722
expt.	−2.0549	−4.7203	−8.4969	−13.386	−19.387	−26.501	−34.731
$1s4p\ ^1P$	−2.0308	−4.6238	−8.2787	−12.996	−18.777	−25.620	−33.526
expt.	−2.0308	−4.6242	−8.2808	−13.000	−18.784	−25.634	−33.548
$1s5p\ ^1P$	−2.0198	−4.5793	−8.1781	−12.816	−18.495	−25.215	−32.974
expt.	−2.0197	−4.5795	−8.1802	−12.821	−18.505	−25.227	−33.000
$1s6p\ ^1P$	−2.0137	−4.5551	−8.1236	−12.719	−18.343	−24.995	−32.675
expt.	−2.0136	−4.5558	−8.1254	−12.724	−18.352	−25.012	−32.701
$1s7p\ ^1P$	−2.0101	−4.5405	−8.0908	−12.661	−18.252	−24.863	−32.495
expt.	−2.0099	−4.5414	−8.0926		−18.261	−24.879	−32.525
$1s8p\ ^1P$	−2.0077	−4.5310	−8.0696	−12.623	−18.192	−24.778	−32.378
expt.	−2.0076				−18.201	−24.787	
$1s9p\ ^1P$	−2.0061	−4.5245	−8.0550	−12.597	−18.152	−24.719	−32.299
expt.	−2.0059						
$1s10p\ ^1P$	−2.0049	−4.5198	−8.0446	−12.579	−18.123	−24.677	−32.241
expt.	−2.0048						
$1s11p\ ^1P$	−2.0040	−4.5164	−8.0368	−12.565	−18.102	−24.646	−32.199
expt.	−2.0039						
$1s12p\ ^1P$	−2.0031	−4.5138	−8.0310	−12.555	−18.085	−24.623	−32.167
expt.	−2.0032						

4. The generalized Slater–Condon rules

The generalized Sturmian method for solving the N-electron Schrödinger equation can be thought of as a direct configuration action method with a special prescription for constructing optimal configurations. These optimal configurations are isoenergetic solutions to the Schrödinger for a system of N electrons in the field of the zeroth-order potential $V_0(\mathbf{x})$ (equation (9)). For rapid convergence, the zeroth-order potential should resemble the actual potential as closely as possible. For the case of atoms and atomic ions, it is possible to solve equation (9) exactly, as we have seen, when $V_0(\mathbf{x})$ is the nuclear attraction potential. The solutions are built up from hydrogenlike atomic spin-orbitals (equation (16)), and they are made isoenergetic by giving each configuration its own effective charge, Q_ν (equation (17)). Because the hydrogenlike spin-orbitals in two different configurations may in general correspond to different effective charges, the spin-orbitals of one configuration are not necessarily orthogonal to those of the other. Therefore, in writing a general program for calculating the spectra of N-electron atoms and ions, we were unable to make use of the usual Slater–Condon rules, and we had to replace these by their generalized form, where orthonormality between different configurations is not assumed. There are many approaches to the generalized Slater–Condon rules [31–35], and therefore, it may be worthwhile to describe the algorithm which, after some experimentation, we found to be the most rapid, direct and robust. The method

Table 4

^1D excited state energies for the two-electron isoelectronic series, compared with experimental values taken from the NIST tables.

	He	Li^+	Be^{2+}	B^{3+}	C^{4+}	N^{5+}	O^{6+}
$1s3d\ ^1D$	−2.0555	−4.7216	−8.4987	−13.387	−19.386	−26.497	−34.719
expt.	−2.0554	−4.7224	−8.5012	−13.392	−19.395	−26.513	−34.745
$1s4d\ ^1D$	−2.0312	−4.6245	−8.2799	−12.997	−18.778	−25.621	−33.527
expt.	−2.0310	−4.6251	−8.2823	−13.003	−18.788	−25.638	−33.555
$1s5d\ ^1D$	−2.0199	−4.5796	−8.1789	−12.818	−18.497	−25.216	−32.975
expt.	−2.0198	−4.5801	−8.1807		−18.506	−25.233	−33.001
$1s6d\ ^1D$	−2.0138	−4.5553	−8.1241	−12.720	−18.344	−24.996	−32.676
expt.	−2.0137	−4.5556			−18.354		−32.703
$1s7d\ ^1D$	−2.0101	−4.5406	−8.0912	−12.661	−18.253	−24.864	−32.496
expt.	−2.0100	−4.5409			−18.262		
$1s8d\ ^1D$	−2.0077	−4.5311	−8.0698	−12.623	−18.193	−24.778	−32.379
expt.	−2.0076	−4.5313			−18.202		
$1s9d\ ^1D$	−2.0061	−4.5246	−8.0551	−12.597	−18.152	−24.720	−32.299
expt.	−2.0059						
$1s10d\ ^1D$	−2.0049	−4.5199	−8.0447	−12.579	−18.123	−24.678	−32.242
expt.	−2.0048						
$1s11d\ ^1D$	−2.0041	−4.5164	−8.0369	−12.565	−18.102	−24.647	−32.200
expt.	−2.0035						
$1s12d\ ^1D$	−2.0033	−4.5138	−8.0310	−12.555	−18.085	−24.623	−32.168
expt.	−2.0032						

Table 5

^2S state energies for the three-electron isoelectronic series, compared with experimental values from the NIST database. Calculated using 137 basis functions in 1.49 s. The energies are all a few tenths of a percent too high.

	Li	Be^+	B^{2+}	C^{3+}	N^{4+}	O^{5+}
$1s^22s\ ^2S$	−7.44844	−14.2889	−23.3842	−34.7320	−48.3311	−64.1811
expt.	−7.47798	−14.3257	−23.4288	−34.7859	−48.3991	−64.2680
$1s^23s\ ^2S$	−7.32865	−13.8937	−22.5709	−33.3599	−46.2609	−61.2735
expt.	−7.35402	−13.9237	−22.6077	−33.4060	−46.3208	−61.3517
$1s^24s\ ^2S$	−7.29358	−13.7714	−22.3119	−32.9149	−45.5805	−60.3090
expt.	−7.31845	−13.7996	−22.3458	−32.9572	−45.6364	−60.3828
$1s^25s\ ^2S$	−7.27780	−13.7184	−22.1975	−32.7164	−45.2751	−59.8740
expt.	−7.30347	−13.7455	−22.2298	−32.7567	−45.3286	−59.9454
$1s^26s\ ^2S$	−7.26143	−13.6872	−22.1361	−32.6108	−45.1127	−59.6422
expt.	−7.29578	−13.7172		−32.6500	−45.1644	−59.7113
$1s^27s\ ^2S$	−7.25117	−13.6611	−22.0907	−32.5404	−45.0098	−59.4990
expt.	−7.29131	−13.7005		−32.5865	−45.0665	−59.5714

which we used in our general program is similar to that described by McWeeny in [34, pp. 61–66]. However, it differed from McWeeny's method by avoiding use of the inverse of the overlap matrix. Thus we avoided problems which arise when the overlap matrix is singular. The method which we used was as follows. Let P be a member of the permutation group for the N-electron system, and let A_N be the antisymmetrizer

$$A_N = \sum_P \varepsilon_P P, \tag{34}$$

ε_P being the sign of the permutation P. In equation (34), A_N is normalized in such a way that instead of strict idempotency, we have

$$A_N^2 = N! A_N. \tag{35}$$

It is convenient to introduce the notation:

$$\begin{aligned}\sqrt{N!}\phi_\nu \equiv F &\equiv \begin{vmatrix} f_1(1) & f_2(1) & \dots & f_N(1) \\ f_1(2) & f_2(2) & \dots & f_N(2) \\ \vdots & \vdots & & \vdots \\ f_1(N) & f_2(N) & \dots & f_N(N) \end{vmatrix} \\ &= A_N f_1(1) f_2(2) \cdots f_N(N) \end{aligned} \tag{36}$$

and

$$\begin{aligned}\sqrt{N!}\phi_{\nu'} \equiv G &\equiv \begin{vmatrix} g_1(1) & g_2(1) & \dots & g_N(1) \\ g_1(2) & g_2(2) & \dots & g_N(2) \\ \vdots & \vdots & & \vdots \\ g_1(N) & g_2(N) & \dots & g_N(N) \end{vmatrix} \\ &= A_N g_1(1) g_2(2) \cdots g_N(N), \end{aligned} \tag{37}$$

where the spin-orbitals in the two configurations ϕ_ν and $\phi_{\nu'}$ are called by different letters to emphasize the fact that the may correspond to different effective charges. Making use of this notation together with equation (35) we can express the scalar product between the two configurations in the form:

$$\begin{aligned}\langle \phi_\nu | \phi_{\nu'} \rangle &= \frac{1}{N!} \langle F | G \rangle \\ &= \frac{1}{N!} \int \mathrm{d}\tau_1 \dots \int \mathrm{d}\tau_N \, \big\{ A_N f_1(1) \cdots f_N(N) \big\}^* \big\{ A_N g_1(1) \cdots g_N(N) \big\} \\ &= \int \mathrm{d}\tau_1 \dots \int \mathrm{d}\tau_N \, f_1^*(1) \cdots f_N^*(N) \big\{ A_N g_1(1) \cdots g_N(N) \big\} \\ &= \int \mathrm{d}\tau_1 \dots \int \mathrm{d}\tau_N \, f_1^*(1) \cdots f_N^*(N) \begin{vmatrix} g_1(1) & g_2(1) & \dots & g_N(1) \\ g_1(2) & g_2(2) & \dots & g_N(2) \\ \vdots & \vdots & & \vdots \\ g_1(N) & g_2(N) & \dots & g_N(N) \end{vmatrix}. \end{aligned} \tag{38}$$

From (38) it can be seen that the scalar product of the two configurations is equal to the determinant of the overlap matrix:

$$\langle \phi_\nu | \phi_{\nu'} \rangle = |S|, \tag{39}$$

where

$$S \equiv \begin{pmatrix} \langle f_1|g_1\rangle & \langle f_1|g_2\rangle & \dots & \langle f_1|g_N\rangle \\ \langle f_2|g_1\rangle & \langle f_2|g_2\rangle & \dots & \langle f_2|g_N\rangle \\ \vdots & \vdots & & \vdots \\ \langle f_N|g_1\rangle & \langle f_N|g_2\rangle & \dots & \langle f_N|g_N\rangle \end{pmatrix}. \tag{40}$$

We next consider matrix elements of one-electron operators of the form

$$V = v(1) + v(2) + \cdots + v(N). \tag{41}$$

The nuclear attraction potential and the kinetic energy operator are examples of operators of this type. Other examples include applied external electric and magnetic fields. From equations (36), (37) and (41) we have

$$\langle \phi_\nu | V | \phi_{\nu'} \rangle = \frac{1}{N!} \langle F|V|G\rangle = \frac{N}{N!} \langle F|v(1)|G\rangle. \tag{42}$$

We next expand the determinants F and G in terms of their minors:

$$F = \sum_{i=1}^{N} (-1)^{i+1} f_i(1) F_i^{N-1} \tag{43}$$

and

$$G = \sum_{j=1}^{N} (-1)^{j+1} g_j(1) G_j^{N-1}. \tag{44}$$

In equation (43), F_i^{N-1} is the minor obtained from the determinant F (equation (36)) by deleting the first row and the ith column. Similarly, in equation (44), G_j^{N-1} is the minor formed from the determinant G by deleting the first row and jth column. Substituting (43) and (44) into (42), we obtain:

$$\langle F|v(1)|G\rangle = \sum_{i=1}^{N} \sum_{j=1}^{N} (-1)^{i+j} \langle f_i|v|g_j\rangle \bigl\langle F_i^{N-1} \bigm| G_j^{N-1} \bigr\rangle, \tag{45}$$

where

$$\langle f_i|v|g_j\rangle \equiv \int \mathrm{d}\tau_1 \, f_i^*(1) v(1) g_j(1). \tag{46}$$

Then, making use of the fact that $A_{N-1}^2 = (N-1)!A_{N-1}$ and following an argument similar to equation (38), we obtain

$$\langle \phi_\nu | V | \phi_{\nu'} \rangle = \sum_{i=1}^{N} \sum_{j=1}^{N} (-1)^{i+j} \langle f_i | v | g_j \rangle |S_{ij}|, \tag{47}$$

where $|S_{ij}|$ is the minor obtained from the determinant of the overlap matrix (equation (40)) by deleting the ith row and the jth column. Finally, we can consider two-electron operators of the type typified by the interelectron repulsion potential. The matrix element of such an operator taken between two N-electron configurations has $N(N-1)/2$ terms, but since the contribution is the same for each of these terms we need only consider one of them, afterwards multiplying by the number of terms. Thus, we can write matrix elements of the interelectron repulsion potential in the form:

$$\langle \phi_\nu | V' | \phi_{\nu'} \rangle = \frac{N(N-1)}{2} \langle \phi_\nu | \frac{1}{r_{12}} | \phi_{\nu'} \rangle = \frac{1}{2(N-2)!} \langle F | \frac{1}{r_{12}} | G \rangle. \tag{48}$$

We now expand the determinants F and G in terms of their double minors:

$$F = \sum_{i=1}^{N} \sum_{j=i+1}^{N} (-1)^{i+j+1} \big[f_i(1) f_j(2) - f_j(1) f_i(2) \big] F_{ij}^{N-2} \tag{49}$$

and

$$G = \sum_{k=1}^{N} \sum_{l=k+1}^{N} (-1)^{k+l+1} \big[g_k(1) g_l(2) - g_l(1) g_k(2) \big] G_{kl}^{N-2}. \tag{50}$$

In equation (49), F_{ij}^{N-2} is the double minor obtained from the determinant F by deleting the first and second rows and the ith and jth columns. The definition of G_{kl}^{N-2} is similar. Then, making use of the fact that $A_{N-2}^2 = (N-2)!A_{N-2}$, and combining equations (48), (49), and (50), we obtain

$$\langle \phi_\nu | V' | \phi_{\nu'} \rangle = \sum_{i=1}^{N} \sum_{j=i+1}^{N} \sum_{k=1}^{N} \sum_{l=k+1}^{N} (-1)^{i+j+k+l} C_{ij;kl} |S_{ij;kl}|, \tag{51}$$

where

$$C_{ij;kl} \equiv \int \mathrm{d}\tau_1 \int \mathrm{d}\tau_2 \, f_i^*(1) f_j^*(2) \frac{1}{r_{12}} \big[g_k(1) g_l(2) - g_l(1) g_k(2) \big]. \tag{52}$$

Equations (39), (42), and (51) are the generalized Slater–Condon rules in the form which we used in our program for calculating the spectra of N-electron atoms.

Thus, the first step in our method is to evaluate the overlap matrix, so that (40) becomes a matrix of numbers. The matrix elements in (39), (42) and (51) can then be evaluated rapidly and directly.

5. The effect of a strong external electric field

Let us now suppose that a uniform external electric field is applied to the atom. Such a field, applied in the direction of the z-axis, can be represented by a potential of the form:

$$V''(\mathbf{x}) = \sum_{j=1}^{N} \mathcal{E} r_j \cos\theta_j. \tag{53}$$

When the effect of the external electric field is taken into account, the generalized Sturmian secular equations for the atom or ion become

$$\sum_{\nu} \left[\delta_{\nu',\nu} Z\mathcal{R} + T'_{\nu',\nu} + \eta T''_{\nu',\nu} - p_0 \delta_{\nu',\nu}\right] B_\nu = 0, \tag{54}$$

where the matrix

$$T''_{\nu',\nu} \equiv -\int \mathrm{d}x\, \phi^*_{\nu'}(\mathbf{x}) \sum_{j=1}^{N} p_0 r_j \cos\theta_j \phi_\nu(\mathbf{x}) \tag{55}$$

is independent of p_0 and where

$$\eta \equiv \frac{\mathcal{E}}{p_0^2}. \tag{56}$$

In equations (53) and (56), $\mathcal{E}$ is the strength of the external electric field expressed in atomic units, i.e., in hartree/bohr. The procedure for calculating the spectrum of an N-electron atom or ion under the influence of a strong external electric field is then as follows. We choose a generalized Sturmian basis set and evaluate the matrices $T'_{\nu',\nu}$ and $T''_{\nu',\nu}$ once and for all. When these matrices have been constructed, almost no effort is required to calculate the effect of many external field strengths on many states, ground and excited, and many values of the nuclear charge Z. For a particular value of Z, we diagonalize the matrices shown in equation (54) for many values of the parameter η. Each diagonalization yields a spectrum of p_0 values, and, through equation (23), a spectrum of energies.

By means of equation (56), we can calculate the value of the external field strength $\mathcal{E}$ to which each of these energies corresponds. In this way, we can plot the spectrum as a function of $\mathcal{E}$, as is shown in figure 1. In this figure the triplet excited states energies of helium, measured in atomic units (hartrees), are shown as functions of the external field strength, also measured in atomic units (hartree/bohr). Only the $M = 0$ energy levels are shown in the figure. 80 generalized Sturmian configurations of the form

$$\phi_\nu(\mathbf{x}) = |\chi_{1,0,0,\frac{1}{2}} \chi_{n,l,0,\frac{1}{2}}|, \qquad n = l+1, \ldots, 16, \qquad l = 0, 1, \ldots, 6, \tag{57}$$

were used in the calculation. In the zero-field limit the excited states shown are dominated respectively by the configurations (starting from the lowest energy) $1s2s$, $1s2p$,

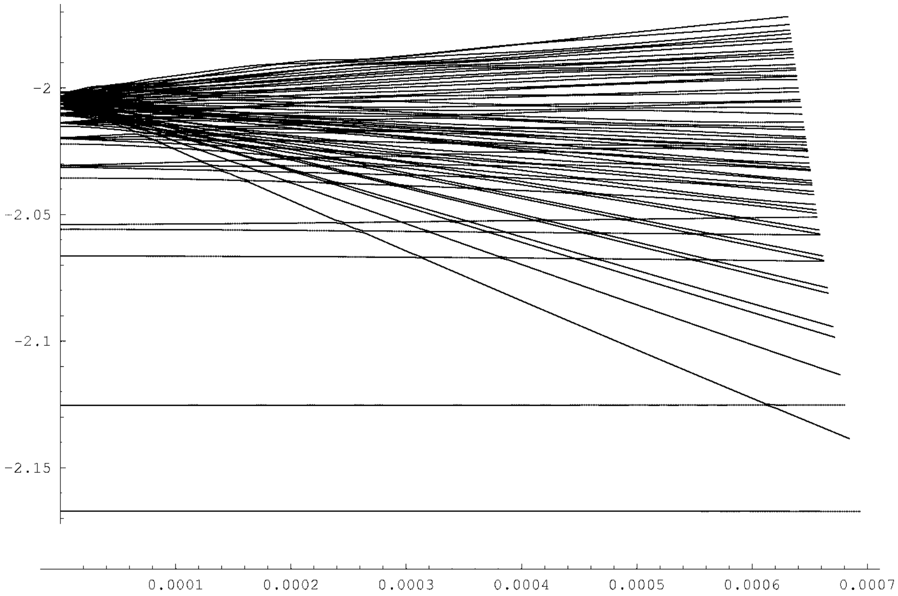

Figure 1. Triplet excited states of helium in a strong external electric field. Both the energies and the field strengths are in atomic units. Only the $M = 0$ states are shown in the figure. A generalized Sturmian basis set with 80 basis functions was used. Besides the expected Stark splitting of the excited states, one can observe in the spectrum a number of anomalous states, whose energy decreases rapidly as the field strength increases. The interpretation of the anomalous states is discussed in the text.

$1s3s$, $1s3p$, $1s3d$, $1s4s$, $1s4p$, $1s4d$, $1s4f$, and so on. In the zero-field limit there is, of course, some mixing of configurations because of the interelectron repulsion term in equation (54), but without the external electric field, configurations corresponding to different values of L do not mix. When the external field is applied, it produces a mixing between configurations corresponding to different values of L, and it also produces the expected Stark splitting. However, in addition to the Stark effect, we can observe in the figure a number of anomalous energy levels, which start near to the ionization limit at zero field strength and which decrease in energy rapidly and almost linearly as the field strength increases. We wished to interpret these anomalous states, and we found that we could do so by making an approximate representation of their wave functions:

$$\psi_\kappa = \sum_\nu \phi_\nu(\mathbf{x}) B_{\nu,\kappa} \approx \begin{vmatrix} \chi_{1,0,0,\frac{1}{2}}(1) & \chi_\kappa(1) \\ \chi_{1,0,0,\frac{1}{2}}(2) & \chi_\kappa(2) \end{vmatrix}, \tag{58}$$

where

$$\chi_\kappa(1) \equiv \sum_\nu \chi_{n,l,0,\frac{1}{2}}(1) B_{\nu,\kappa}. \tag{59}$$

This approximation assumes that we can ignore changes in $\chi_{1,0,0,\frac{1}{2}}$ due to the fact that each configuration has its own effective nuclear charge, Q_ν (equation (17)). Although the approximation is a crude one, it allows us to interpret the anomalous states. Figure 2

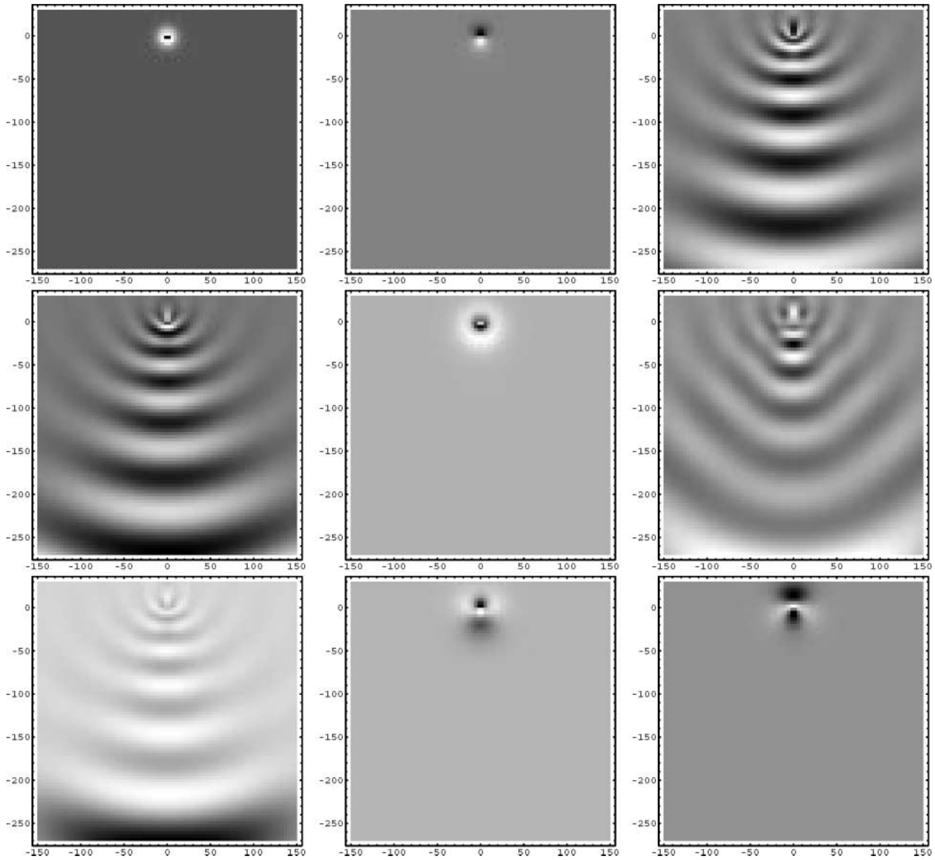

Figure 2. This figure shows cross-sections of the wave function for the first nine states of a He atom experiencing a field strength of $4.5 \cdot 10^{-5}$ hartree/bohr. The scale of the figures is such that the domain of the atom occupies only a small part of the figure, as can be seen from the normal states (state 1, 2, 5, 8 and 9). Thus, the orbitals of the anomalous states are those of electrons which are outside of the atom, only a small part of the wavefunctions being inside it. With a larger basis set, the orbital part would extend still further from the atom. In other words, the orbitals are those of ionized electrons in the field of the nucleus and the remaining bound electron.

shows χ_κ, equation (40), for the lowest-energy anomalous state shown in figure 1. The external field is in the z direction, and figure 2 shows a plot of the orbital χ_κ in the x–z plane. The scale is such that size of the helium atom in its ground state is very small in comparison to the size of the figure. Thus, the anomalous orbital is seen to be localized primarily outside the domain of the atom, with only a small amplitude inside. The anomalous states are thus seen to be states in which one of the electrons has escaped from the atom because of the effect of the external field, while the other electron remains bound to the nucleus. Our 80-configuration generalized Sturmian basis set, equation (57), was large enough to give us an approximate representation of these ionized states.

We then investigated the effect of increasing or decreasing the size of the basis set. The effect was dramatic. When the basis set was increased, the number of anomalous states increased and the slope of their lines on the graph became much greater. Conversely, when the size of the basis set was decreased, the slope became smaller. These results were easy to interpret: a large basis set allowed the ionized orbital to be represented far from the atom, in regions where the potential well due to the external electric field becomes very deep. The farther out one is able to represent the state, the more sensitive its energy becomes to the field strength. While the Stark splitting converged to a well-defined limit with an increasing basis set, the energies of the ionized states remained strongly basis-set dependent, no matter how large the basis became. This result was a little discouraging because, having obtained the ionized states, one would like to use them to calculate the results of the following experiment: suppose that an atom is placed in a strong uniform electric field. We then illuminate the atom with light of variable frequency and observe the rate of ionization as a function of frequency, thus obtaining an “action spectrum” for the photoionization Stark effect. The action spectrum might then be measured for other values of the field strength. We hope to return to this problem in another publication. Our hope is that it may be possible to reach basis-set-independent results by means of box normalization.

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