The generalized Sturmian method and inelastic scattering of fast electrons

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The generalized Sturmian method for solving the many-electron Schrödinger equation is reviewed. This method yields rapidly convergent solutions directly, without the use of the SCF approximation. As a simple illustrative example, differential cross sections are calculated for inelastic scattering of fast electrons by atoms and ions in the 2-electron isoelectronic series.

KEY WORDS: generalized Sturmians, inelastic scattering, excitation, quantum theory, atomic structure

1. Introduction

The generalized Sturmian method [1–9] is a form of direct configuration interaction, with a special prescription for constructing optimal configurations. The method offers several advantages. The kinetic energy term disappears from the secular equation; the nuclear attraction term is already diagonal; the optimal Slater exponents are given automatically; a rapidly convergent solution to the many-electron Schrödinger equation can be obtained directly, without the use of the SCF approximation; and excited states can be calculated accurately [7].

Generalized Sturmians are similar to the familiar Sturmian basis sets of atomic and molecular physics [10–15] in that they are solutions to a Schrödinger equation with a weighted "basis potential", the weighting factor being chosen in such a way that all the members of the basis set correspond to the same value of the energy, E. In the case of generalized Sturmian basis sets, all the members of a set satisfy

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

where $\mathbf{x}$ is a $3N$-dimensional vector representing the coordinates of the electrons and β_ν is a weighting factor especially chosen so that all the members of the basis set correspond to the same energy.

The method can be used to study the electronic structure and properties both of atoms and of molecules [7]. When the method is applied to atoms, it is convenient to let $V_0(\mathbf{x})$ be the attractive potential of the nucleus:

$$V_0(\mathbf{x}) = -\sum_{j=1}^{N} \frac{Z}{r_j}. \tag{2}$$

Then solutions to equation (1) can be built up from the familiar hydrogen-like atomic spin-orbitals:

$$\chi_\mu(j) = R_{nl}(r_j) Y_{lm}(\theta_j, \phi_j) \begin{cases} \alpha(j) \\ \beta(j) \end{cases}, \tag{3}$$

where α and β are spin functions, Y_{lm} is a spherical harmonic, and

$$R_{nl}(r) = \mathcal{N}_{nl} \left(\frac{2Q_v r}{n} \right)^l e^{-Q_v r/n} F(l+1-n|2l+2|2Q_v r/n),$$

$$\mathcal{N}_{nl} = \frac{2(Q_v/n)^{3/2}}{(2l+1)!} \sqrt{\frac{(l+n)!}{n(n-l-1)!}}. \tag{4}$$

In equation (4), $F(a|b|x) \equiv 1 + ax/b + a(a+1)x^2/(b(b+1)2!) + \cdots$ is a confluent hypergeometric function while $Q_v = \beta_v Z$ is an effective charge. The hydrogen-like atomic spin-orbitals $\chi_\mu(j)$ satisfy the one-electron Schrödinger equation:

$$\left[-\frac{1}{2} \nabla_j^2 - \frac{Q_v}{r_j} + \frac{1}{2} \left(\frac{Q_v}{n} \right)^2 \right] \chi_\mu(j) = 0. \tag{5}$$

If we let

$$\phi_v(\mathbf{x}) \equiv |\chi_\mu \chi_{\mu'} \chi_{\mu''} \cdots| \equiv \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_\mu(1) & \chi_{\mu'}(1) & \chi_{\mu''}(1) & \cdots \\ \chi_\mu(2) & \chi_{\mu'}(2) & \chi_{\mu''}(2) & \cdots \\ \vdots & \vdots & & \vdots \\ \chi_\mu(N) & \chi_{\mu'}(N) & \chi_{\mu''}(N) & \cdots \end{vmatrix}, \tag{6}$$

then from equation (5) we have

$$\left[-\sum_{j=1}^{N} \frac{1}{2} \nabla_j^2 \right] \phi_v(\mathbf{x}) = \left[\frac{Q_v}{r_1} - \frac{1}{2} \left(\frac{Q_v}{n} \right)^2 + \frac{Q_v}{r_2} - \frac{1}{2} \left(\frac{Q_v}{n'} \right)^2 + \cdots \right] \phi_v(\mathbf{x})$$

$$= \left[-\beta_v V_0(\mathbf{x}) - \frac{Q_v^2}{2} \left(\frac{1}{n^2} + \frac{1}{n'^2} + \frac{1}{n''^2} + \cdots \right) \right] \phi_v(\mathbf{x}), \tag{7}$$

where

$$E = -\frac{Q_v^2}{2} \left(\frac{1}{n^2} + \frac{1}{n'^2} + \frac{1}{n''^2} + \cdots \right). \tag{8}$$

Thus, provided that we choose the effective charge Q_ν (and hence, $\beta_\nu = Q_\nu/Z$) in such a way that equation (8) is satisfied, the configuration $\phi_\nu(\mathbf{x})$ will satisfy equation (1). If we introduce the parameters p_0 and $\mathcal{R}_\nu$ with the definitions

$$E \equiv -\frac{p_0^2}{2} \tag{9}$$

and

$$\mathcal{R}_\nu \equiv \left(\frac{1}{n^2} + \frac{1}{n'^2} + \frac{1}{n''^2} + \cdots \right)^{1/2}, \tag{10}$$

then the subsidiary condition (8) can be rewritten in the form:

$$p_0 = Q_\nu \mathcal{R}_\nu. \tag{11}$$

The parameter p_0 is the same for all the generalized Sturmian configurations in a basis set (since all correspond to the same energy), while the effective charge Q_ν and the radical $\mathcal{R}_\nu$ characterize a particular configuration, $\phi_\nu(\mathbf{x})$.

2.   Potential-weighted orthonormality

Generalized Sturmian basis functions, constructed in the way just described, obey potential-weighted orthonormality relations. To see this, consider two different functions, both corresponding to the same energy, obeying respectively

$$\left[\frac{1}{2} \sum_{j=1}^{N} \nabla_j^2 + E \right] \phi_\nu(\mathbf{x}) = \beta_\nu V_0(\mathbf{x}) \phi_\nu(\mathbf{x}) \tag{12}$$

and

$$\left[\frac{1}{2} \sum_{j=1}^{N} \nabla_j^2 + E \right] \phi_{\nu'}(\mathbf{x}) = \beta_{\nu'} V_0(\mathbf{x}) \phi_{\nu'}(\mathbf{x}). \tag{13}$$

Then

$$\int \mathrm{d}x\, \phi_{\nu'}^*(\mathbf{x}) \left[\frac{1}{2} \sum_{j=1}^{N} \nabla_j^2 + E \right] \phi_\nu(\mathbf{x}) = \beta_\nu \int \mathrm{d}x\, \phi_{\nu'}^*(\mathbf{x}) V_0(\mathbf{x}) \phi_\nu(\mathbf{x}) \tag{14}$$

and

$$\int \mathrm{d}x\, \phi_\nu^*(\mathbf{x}) \left[\frac{1}{2} \sum_{j=1}^{N} \nabla_j^2 + E \right] \phi_{\nu'}(\mathbf{x}) = \beta_{\nu'} \int \mathrm{d}x\, \phi_\nu^*(\mathbf{x}) V_0(\mathbf{x}) \phi_{\nu'}(\mathbf{x}). \tag{15}$$

If we take the complex conjugate of (15) and subtract it from (14), making use of the Hermiticity of the operator on the left, we obtain

$$(\beta_\nu - \beta_{\nu'}) \int \mathrm{d}x\, \phi_{\nu'}^*(\mathbf{x}) V_0(\mathbf{x}) \phi_\nu(\mathbf{x}) = 0, \tag{16}$$

so that if $\beta_\nu \neq \beta_{\nu'}$,

$$\int dx\, \phi_{\nu'}^*(\mathbf{x}) V_0(\mathbf{x}) \phi_\nu(\mathbf{x}) = 0. \tag{17}$$

Orthogonality with respect to the minor quantum numbers, on which the energy does not depend, follows from the orthonormality of the spin functions and the spherical harmonics. The normalization of the basis set can be established from the fact that the familiar atomic spin-orbitals, defined by equations (3) and (4), obey

$$\int d^3x_j \left| \chi_\mu(j) \right|^2 \frac{1}{r_j} = \frac{Q_\nu}{n^2}. \tag{18}$$

Making use of the Slater–Condon rules and equation (11) we have:

$$\int dx\, |\phi_\nu(\mathbf{x})|^2 V_0(\mathbf{x}) = -\sum_{\mu \subset \nu} \int d^3x_j \left| \chi_\mu(\mathbf{x}_j) \right|^2 \frac{Z}{r_j} = -\frac{Z}{Q_\nu} Q_\nu^2 \mathcal{R}_\nu^2 = -\frac{p_0^2}{\beta_\nu}. \tag{19}$$

Thus, the potential-weighted orthonormality relation becomes:

$$\int dx\, \phi_{\nu'}^*(\mathbf{x}) V_0(\mathbf{x}) \phi_\nu(\mathbf{x}) = -\delta_{\nu',\nu} \frac{p_0^2}{\beta_\nu}. \tag{20}$$

3.   The secular equation

Having constructed our basis set, we would like to use it to solve the many-electron Schrödinger equation:

$$\left[-\frac{1}{2} \sum_{j=1}^N \nabla_j^2 + V(\mathbf{x}) - E \right] \psi(\mathbf{x}) = 0, \tag{21}$$

where

$$V(\mathbf{x}) = V_0(\mathbf{x}) + V'(\mathbf{x}) \tag{22}$$

and where $V'(\mathbf{x})$ is the interelectron repulsion potential

$$V'(\mathbf{x}) = \sum_{i>j}^N \sum_{j=1}^N \frac{1}{r_{ij}}. \tag{23}$$

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

$$\sum_\nu \left[-\frac{1}{2} \sum_{j=1}^N \nabla_j^2 + V(\mathbf{x}) - E \right] \phi_\nu(\mathbf{x}) B_\nu = 0. \tag{24}$$

Since each configuration in the basis satisfies (1), equation (24) can be rewritten in the form

$$\sum_\nu \left[V(\mathbf{x}) - \beta_\nu V(\mathbf{x}) \right] \phi_\nu(\mathbf{x}) B_\nu = 0. \tag{25}$$

Multiplying (25) by a conjugate function from the basis set and integrating over the coordinates, making use of the potential-weighted orthonormality relations yields:

$$\sum_\nu \left[\int d x \, \phi_{\nu'}^*(\mathbf{x}) V(\mathbf{x}) \phi_\nu(\mathbf{x}) + p_0^2 \delta_{\nu',\nu} \right] B_\nu = 0. \tag{26}$$

We now introduce the definition:

$$T_{\nu',\nu} \equiv -\frac{1}{p_0} \int d x \, \phi_{\nu'}^*(\mathbf{x}) V(\mathbf{x}) \phi_\nu(\mathbf{x}). \tag{27}$$

The minus in this definition is motivated by the fact that $V(\mathbf{x})$ is predominantly an attractive potential. We divide by p_0 because when $V(\mathbf{x})$ involves only Coulomb forces, $T_{\nu',\nu}$ is then independent of p_0. With this definition of $T_{\nu',\nu}$, equation (26) becomes

$$\sum_\nu \left[T_{\nu',\nu} - p_0 \delta_{\nu',\nu} \right] B_\nu = 0. \tag{28}$$

The matrix $T_{\nu',\nu}$ consists of two terms, one representing nuclear attraction, and the other interelectronic repulsion. The nuclear attraction term is diagonal because of the potential-weighted orthonormality relation (20):

$$T_{\nu',\nu}^0 \equiv -\frac{1}{p_0} \int d x \, \phi_{\nu'}^*(\mathbf{x}) V_0(\mathbf{x}) \phi_\nu(\mathbf{x}) = \delta_{\nu',\nu} \frac{p_0}{\beta_\nu} = \delta_{\nu',\nu} Z \mathcal{R}_\nu. \tag{29}$$

Thus, finally, the generalized Sturmian secular equation for an N-electron atom becomes

$$\sum_\nu \left[T_{\nu',\nu}' + Z \mathcal{R}_\nu \delta_{\nu',\nu} - p_0 \delta_{\nu',\nu} \right] B_\nu = 0, \tag{30}$$

where

$$T_{\nu',\nu}' \equiv -\frac{1}{p_0} \int d x \, \phi_{\nu'}^*(\mathbf{x}) \sum_{i>j}^N \sum_{j=1}^N \frac{1}{r_{ij}} \phi_\nu(\mathbf{x}). \tag{31}$$

The secular equation (30) has several interesting features. The kinetic energy term has disappeared; the nuclear attraction term is diagonal; and the roots are not energies, but values of the parameter p_0, which is related to the energy by equation (9).

4.   Inelastic scattering of fast electrons

As a simple example to illustrate the generalized Sturmian method, we can apply it to the inelastic scattering of fast electrons by atoms and ions. The following formula

for the differential inelastic scattering cross section in the Born approximation was first derived by Bethe [16]. In atomic units,

$$\frac{\mathrm{d}\sigma_v}{\mathrm{d}\Omega} \approx \left(\frac{4k'}{kq^4}\right) \left| \int \mathrm{d}x \sum_{j=1}^{N} \mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{x}_j} \psi_0^* \psi_v \right|^2. \tag{32}$$

In equation (32), $\mathbf{k}$ is the momentum of the incident electron, $\mathbf{k}'$ is the momentum of the inelasticly scattered electron, while $\mathbf{q}$ is the momentum transfered to the scatterer. The initial and final states of the scatterer are represented respectively by ψ_0 and ψ_v. If ΔE is the positive energy difference between ψ_v and ψ_0, then conservation of energy requires that

$$k'^2 = k^2 - 2\Delta E, \tag{33}$$

while conservation of momentum yields the requirement

$$\mathbf{k} - \mathbf{k}' = \mathbf{q}. \tag{34}$$

Thus,

$$q^2 = \left(\mathbf{k} - \mathbf{k}'\right) \cdot \left(\mathbf{k} - \mathbf{k}'\right) = 2k^2 - 2\Delta E - 2k\sqrt{k^2 - 2\Delta E} \cos\theta, \tag{35}$$

where

$$\cos\theta \equiv \frac{\mathbf{k} \cdot \mathbf{k}'}{kk'}. \tag{36}$$

In order to calculate the differential cross section, we can use the generalized Sturmian method to evaluate ψ_0, ψ_v and ΔE and substitute them into equations (32), (33) and (35). For example, let us consider inelastic scattering of fast electrons by atoms and ions of the two-electron isoelectronic series: He, Li^+, Be^{2+}, B^{3+}, C^{4+}, etc. For simplicity, we shall use the approximation where the wave function is represented by a single configuration. (Higher accuracy could, of course, be obtained by using many configurations.) Then the singlet ground state has the form

$$\psi_0 \approx \chi_{1s}(\mathbf{x}_1)\chi_{1s}(\mathbf{x}_2)\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right], \tag{37}$$

where

$$\chi_{1s}(\mathbf{x}_1) = \frac{1}{\sqrt{\pi}}Q_0^{3/2}\mathrm{e}^{-Q_0 r}. \tag{38}$$

The effective charge Q_0 characterizing the ground state configuration can be found from the secular equation (30). Since we are approximating the state by a single configuration, the secular equation reduces to [5,7]

$$p_0 = Z\mathcal{R}_0 + T'_{0,0} = Z\sqrt{\frac{1}{1} + \frac{1}{1}} - 0.441942, \tag{39}$$

where Z is the nuclear charge. Then from equation (11) we have

$$Q_0 = \frac{p_0}{\mathcal{R}_0} = Z - 0.312500. \tag{40}$$

If we approximate singlet excited states by a single configuration then we can write

$$\psi_\nu \approx \frac{1}{2}\big[\chi_{1s'}(\mathbf{x}_1)\chi_{nlm}(\mathbf{x}_2) + \chi_{nlm}(\mathbf{x}_1)\chi_{1s'}(\mathbf{x}_2)\big]\big[\alpha(1)\beta(2) - \beta(1)\alpha(2)\big], \tag{41}$$

where

$$\chi_{1s'}(\mathbf{x}_1) = \frac{1}{\sqrt{\pi}} Q_{nl}^{3/2} e^{-Q_{nl}r_1}, \tag{42}$$

while χ_{nlm} can be written in the form

$$\chi_{nlm}(\mathbf{x}_2) = Y_{lm}(\hat{\mathbf{x}}_2)e^{-Q_{nl}r_2/n}\sum_k C_k r_2^k. \tag{43}$$

The matrix element in equation (32) then becomes:

$$\int dx \sum_{j=1}^2 e^{i\mathbf{q}\cdot\mathbf{x}_j}\psi_0\psi_\nu = \frac{1}{\sqrt{2}}\int d^3x_1 \int d^3x_2 \sum_{j=1}^2 e^{i\mathbf{q}\cdot\mathbf{x}_j}\chi_{1s}(\mathbf{x}_1)\chi_{1s}(\mathbf{x}_2)$$
$$\times\big[\chi_{1s'}(\mathbf{x}_1)\chi_{nlm}(\mathbf{x}_2) + \chi_{nlm}(\mathbf{x}_1)\chi_{1s'}(\mathbf{x}_2)\big]. \tag{44}$$

If $l \neq 0$, this reduces to

$$\int dx \sum_{j=1}^2 e^{i\mathbf{q}\cdot\mathbf{x}_j}\psi_0\psi_\nu = \sqrt{2}\int d^3x_1 \, \chi_{1s}(\mathbf{x}_1)\chi_{1s'}(\mathbf{x}_1) \int d^3x_2 \, e^{i\mathbf{q}\cdot\mathbf{x}_2}\chi_{1s}(\mathbf{x}_2)\chi_{nlm}(\mathbf{x}_2). \tag{45}$$

We now introduce the expansion of a plane wave in terms of spherical harmonics and spherical Bessel functions:

$$e^{i\mathbf{q}\cdot\mathbf{x}_2} = 4\pi\sum_{l=0}^\infty i^l j_l(qr_2)\sum_{m=-l}^l Y_{lm}(\hat{\mathbf{q}})Y_{lm}^*(\hat{\mathbf{x}}_2). \tag{46}$$

From (42), (43), (46), and from the orthonormality of the spherical harmonics, we have

$$\int d^3x_2 \, e^{i\mathbf{q}\cdot\mathbf{x}_2}\chi_{1s}(\mathbf{x}_2)\chi_{nlm}(\mathbf{x}_2)$$
$$= 4\sqrt{\pi}i^l Y_{lm}(\hat{\mathbf{q}})Q_0^{3/2}\sum_k C_k \int_0^\infty dr_2 \, r_2^{2+k} j_l(qr_2)e^{-(Q_0+Q_{nl}/n)r_2}. \tag{47}$$

Integrals of the form

$$J_{\kappa,l}(q,\zeta) \equiv \int_0^\infty dr \, r^\kappa j_l(qr)e^{-\zeta r} \tag{48}$$

Table 1

$$J_{\kappa,l}(q, \zeta) \equiv \int_0^\infty dr\, r^\kappa e^{-\zeta r} j_l(qr).$$

l	$J_{1,l}$	$J_{2,l}$	$J_{3,l}$	$J_{4,l}$
0	$\dfrac{1}{q^2 + \zeta^2}$	$\dfrac{2\zeta}{(q^2 + \zeta^2)^2}$	$\dfrac{2(3\zeta^2 - q^2)}{(q^2 + \zeta^2)^3}$	$\dfrac{24\zeta(\zeta^2 - q^2)}{(q^2 + \zeta^2)^4}$
1		$\dfrac{2q}{(q^2 + \zeta^2)^2}$	$\dfrac{8q\zeta}{(q^2 + \zeta^2)^3}$	$\dfrac{8q(5\zeta^2 - q^2)}{(q^2 + \zeta^2)^4}$
2			$\dfrac{8q^2}{(q^2 + \zeta^2)^3}$	$\dfrac{48q^2\zeta}{(q^2 + \zeta^2)^4}$
3				$\dfrac{48q^3}{(q^2 + \zeta^2)^4}$

are easy to evaluate [7]. The first few of these integrals are shown in table 1. They obey the recursion relation

$$J_{\kappa+1,l}(q, \zeta) = -\frac{\partial}{\partial \zeta} J_{\kappa,l}(q, \zeta), \tag{49}$$

and the integrals $J_{l+1,l}$ have the general form

$$J_{l+1,l}(q, \zeta) = \frac{2^l l! q^l}{(q^2 + \zeta^2)^{l+1}}. \tag{50}$$

Equations (49) and (50) allow us to generate all the needed integrals. The remaining factor in equation (45) is

$$\sqrt{2} \int d^3x_1\, \chi_{1s}(\mathbf{x}_1)\chi_{1s'}(\mathbf{x}_1) = \frac{8\sqrt{2}(Q_0 Q_{nl})^{3/2}}{(Q_0 + Q_{nl})^3}. \tag{51}$$

In equations (42)–(51), Q_{nl} is the effective charge associated with the excited configuration of the atom or ion. We can find Q_{nl} by solving the secular equation (30), which reduces to

$$p_0 = Z\mathcal{R}_\nu + T'_{\nu,\nu}. \tag{52}$$

When $n = 2$ and $l = 1$, this becomes [5]

$$p_0 = Z\sqrt{\frac{1}{1} + \frac{1}{4}} - 0.201897, \tag{53}$$

so that

$$Q_{2,1} = \frac{p_0}{\mathcal{R}_{2,1}} = Z - 0.180582. \tag{54}$$

In this example, equation (43) becomes:

$$\chi_{21m}(\mathbf{x}_2) = Y_{1m}(\hat{\mathbf{x}}_2)e^{-Q_{2,1}r_2/2}\frac{2}{\sqrt{3}}\left(\frac{Q_{2,1}}{2}\right)^{5/2} r_2, \tag{55}$$

so that, from (47)–(50),

$$\int d^3x_2\, e^{i\mathbf{q}\cdot\mathbf{x}_2}\chi_{1s}(\mathbf{x}_2)\chi_{21m}(\mathbf{x}_2) = 4\sqrt{\pi}\,i^l Y_{1m}(\hat{\mathbf{q}})Q_0^{3/2}\frac{2}{\sqrt{3}}\left(\frac{Q_{2,1}}{2}\right)^{5/2}\frac{8q\zeta}{(q^2+\zeta^2)^3}, \quad (56)$$

where

$$\zeta = Q_0 + \frac{Q_{2,1}}{2}. \tag{57}$$

For $n = 3$ and $l = 1$ [5]

$$p_0 = Z\sqrt{\frac{1}{1}+\frac{1}{9}} - 0.107540, \tag{58}$$

so that the effective charge is given by

$$Q_{3,1} = \frac{p_0}{\mathcal{R}_{3,1}} = Z - 0.102021. \tag{59}$$

The differential cross sections $d\sigma_{21m}/d\Omega$ and $d\sigma_{31m}/d\Omega$, calculated in the way just described, are exhibited in tables 2 and 3 for the 2-electron isoelectronic series. (The cross sections are labeled with the subscript $\{nlm\}$.) Figures 1 and 2 show these cross sections for He, for $k = 100$ and $k = 150$. One can see from these figures that as k increases, the differential cross sections become more sharply peaked in the region of small θ. Calculation of the total cross sections shows that they decrease with increasing k. Figure 3 shows $d\sigma_{210}/d\Omega$, $d\sigma_{310}/d\Omega$ and $d\sigma_{410}/d\Omega$ for helium. One can see from this figure that the differential cross sections for inelastic scattering of fast electrons decrease with increasing values of n. The total cross sections decrease as Z increases and also as k increases, as is illustrated in table 4.

For $\Delta L = 1$, the inelastic scattering cross sections are very large at small values of θ, while for other values of ΔL, the total cross sections are smaller and the differential cross sections are less sharply peaked at small values of θ. This property can be understood by considering equations (32) and (35), since we are considering the inelastic scattering of fast electrons, $\Delta E/k^2 \ll 1$, and we can expand the square root in equation (35) as a Taylor series in this parameter. If we do this, making use of the identity $1 - \cos\theta = 2\sin^2(\theta/2)$ we obtain

$$q^2 \approx 4(k^2 - \Delta E)\sin^2(\theta/2) + \left(\frac{\Delta E}{k}\right)^2\cos\theta. \tag{60}$$

Thus, for $\theta \ll 1$ we have the approximate relationship:

$$q^2 \approx k^2\theta^2 + \left(\frac{\Delta E}{k}\right)^2, \tag{61}$$

where, from equations (9), (39) and (52),

$$\Delta E \approx \frac{1}{2}\left[\left(Z\mathcal{R}_0 + T'_{0,0}\right)^2 - \left(Z\mathcal{R}_\nu + T'_{\nu,\nu}\right)^2\right]. \tag{62}$$

Table 2

	$\dfrac{d\sigma_{2,1,0}}{d\Omega}$	$\dfrac{d\sigma_{2,1,\pm 1}}{d\Omega}$
He	$\dfrac{1.6474 \times 10^5 k' \cos^2 \theta_q}{kq^2(q^2 + 6.7455)^6}$	$\dfrac{8.2372 \times 10^4 k' \sin^2 \theta_q}{kq^2(q^2 + 6.7455)^6}$
Li$^+$	$\dfrac{1.4836 \times 10^7 k' \cos^2 \theta_q}{kq^2(q^2 + 16.787)^6}$	$\dfrac{7.4180 \times 10^6 k' \sin^2 \theta_q}{kq^2(q^2 + 16.787)^6}$
Be^{2+}	$\dfrac{3.2656 \times 10^8 k' \cos^2 \theta_q}{kq^2(q^2 + 31.329)^6}$	$\dfrac{1.6328 \times 10^8 k' \sin^2 \theta_q}{kq^2(q^2 + 31.329)^6}$
B^{3+}	$\dfrac{3.4511 \times 10^9 k' \cos^2 \theta_q}{kq^2(q^2 + 50.370)^6}$	$\dfrac{1.7256 \times 10^9 k' \sin^2 \theta_q}{kq^2(q^2 + 50.370)^6}$
C^{4+}	$\dfrac{2.3224 \times 10^{10} k' \cos^2 \theta_q}{kq^2(q^2 + 73.912)^6}$	$\dfrac{1.1612 \times 10^{10} k' \sin^2 \theta_q}{kq^2(q^2 + 73.912)^6}$
N^{5+}	$\dfrac{1.1509 \times 10^{11} k' \cos^2 \theta_q}{kq^2(q^2 + 101.95)^6}$	$\dfrac{5.7545 \times 10^{10} k' \sin^2 \theta_q}{kq^2(q^2 + 101.95)^6}$

Table 3

	$\dfrac{d\sigma_{3,1,0}}{d\Omega} = 2\cot^2\theta_q \dfrac{d\sigma_{3,1,\pm 1}}{d\Omega}$
He	$\dfrac{7.3196 \times 10^4 k' (q^2 + 1.5079)^2 \cos^2 \theta_q}{kq^2(q^2 + 5.3831)^8}$
Li$^+$	$\dfrac{6.0770 \times 106 k' (q^2 + 3.9324)^2 \cos^2 \theta_q}{kq^2(q^2 + 13.348)^8}$
Be^{2+}	$\dfrac{1.2858 \times 10^8 k' (q^2 + 7.6703)^2 \cos^2 \theta_q}{kq^2(q^2 + 24.868)^8}$
B^{3+}	$\dfrac{1.3274 \times 10^9 k' (q^2 + 12.529)^2 \cos^2 \theta_q}{kq^2(q^2 + 39.944)^8}$
C^{4+}	$\dfrac{8.7958 \times 10^9 k' (q^2 + 18.574)^2 \cos^2 \theta_q}{kq^2(q^2 + 58.576)^8}$
N^{5+}	$\dfrac{4.3114 \times 10^{10} k' (q^2 + 25.803)^2 \cos^2 \theta_q}{kq^2(q^2 + 80.763)^8}$

Equation (61) tells us that when θ is very small, q is also small, and it is then valid to expand the plane wave in (32) in a Taylor series:

$$e^{i\mathbf{q}\cdot\mathbf{x}_j} = 1 + i\mathbf{q}\cdot\mathbf{x}_j - \frac{1}{2}(\mathbf{q}\cdot\mathbf{x}_j)^2 + \cdots . \tag{63}$$

The monopole term in this series vanishes in (32) because of the orthonormality between ψ_0 and ψ_ν. When $\Delta L = 1$ for a transition, it is "dipole allowed", and the leading
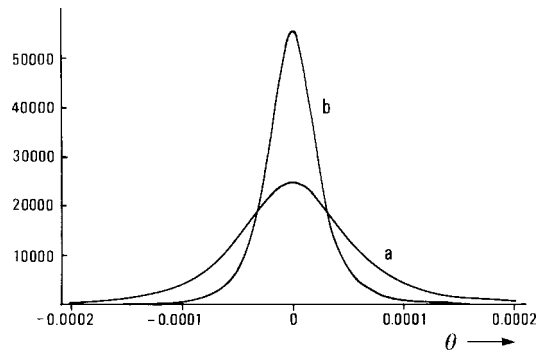
Figure 1. $d\sigma_{2,1,0}/d\Omega$ for helium as a function of the angle θ between $\mathbf{k}$ and $\mathbf{k}'$. Curve (a) corresponds to $k = 100$, while (b) corresponds to $k = 150$. Atomic units are used throughout, except that θ is expressed in radians.
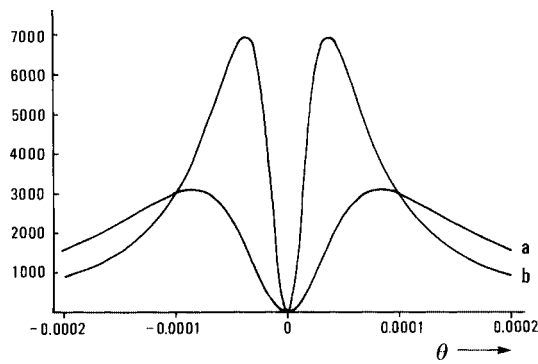

Figure 2. $d\sigma_{2,1,\pm1}/d\Omega$ for helium as a function of θ. Curve (a) corresponds to $k = 100$, while (b) corresponds to $k = 150$.
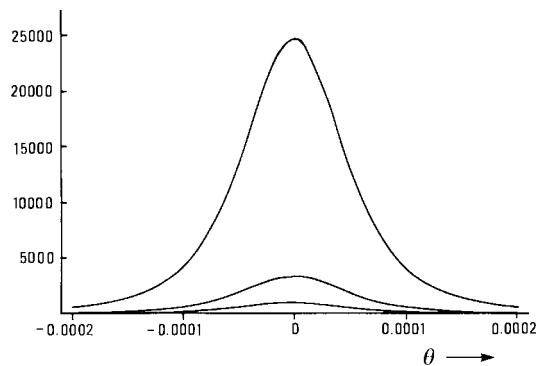

Figure 3. This figure illustrates the decrease in magnitude of the differential cross sections for inelastic scattering as the principal quantum number of the excited state increases. The figure shows $d\sigma_{2,1,0}/d\Omega$ (largest), $d\sigma_{3,1,0}/d\Omega$ (smaller), and $d\sigma_{4,1,0}/d\Omega$ (smallest) for helium with $k = 100$ atomic units.

Table 4
Total cross sections in atomic units.

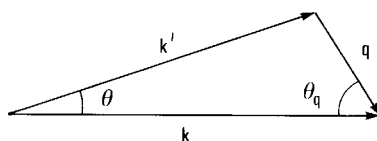| k	$\sigma_{2,1,\pm1}$(He)	$\sigma_{2,1,0}$(He)	$\sigma_{2,1,\pm1}$(Li$^+$)	$\sigma_{2,1,0}$(Li$^+$)
25	0.0037533	0.0013690	0.0011293	0.0005213
50	0.0011686	0.0003441	0.0003727	0.0001307
75	0.0005822	0.0001515	0.0001888	0.0000583
100	0.0003478	0.0000854	0.0001155	0.0000327
150	0.0001703	0.0000381	0.0000570	0.0000146
200	0.0001006	0.0000215	0.0000340	0.0000081

Figure 4. This figure illustrates the geometry of $\mathbf{k}$, the momentum of the incident fast electron, $\mathbf{k}'$, its momentum after inelastic scattering, and $\mathbf{q}$, the momentum transfered to the scatterer. θ is the angle between $\mathbf{k}$ and $\mathbf{k}'$, while $\theta_q = \arcsin(k'\sin\theta/q)$ is the angle between $\mathbf{q}$ and $\mathbf{k}$. Because of the inelasticity of the process, $k' = \sqrt{k^2 - 2\Delta E}$ is slightly smaller than k.

contribution to (32) comes from the the dipole term, $i\mathbf{q}\cdot\mathbf{x}_j$, in (63). For small values of q the factor $|\int dx \sum_j e^{i\mathbf{q}\cdot\mathbf{x}_j}\psi_0^*\psi_\nu|^2$ in (32) is then proportional to q^2. This means that for small values of θ and q, the cross sections corresponding to dipole-allowed transitions are proportional to q^{-2}, a factor which becomes extremely large in the forward direction. By contrast, $\Delta L = 0$ corresponds to a dipole-forbidden transition. In this case, the leading term in the Taylor series is the quadrupole term, and $|\int dx \sum_j e^{i\mathbf{q}\cdot\mathbf{x}_j}\psi_0^*\psi_\nu|^2$ is proportional to q^4 when q is small. This is sufficient to cancel the q^{-4} in the factor $(4k'/(kq^4))$, with the result that the total cross section is small, and the differential cross section is less sharply peaked in the forward direction. Differential cross sections for the 1-electron isoelectronic series are shown for comparison in table 5, and these cross sections also exhibit the characteristics just discussed.

5.   Discussion

The generalized Sturmian method provides an interesting and fresh alternative to the usual SCF-CI methods for calculating the electronic structure and properties of atoms and molecules. As we mentioned above, the method is a form of direct configuration interaction, with a special prescription for the construction of optimum configurations. In the present paper, we have used the single configuration approximation for the sake of simplicity, but higher accuracy could be obtained by using more configurations. Usually in a multiconfigurational generalized Sturmian calculation, a given degree of accuracy can be obtained with far fewer configurations than are needed in conventional methods.

Table 5
Cross sections for the 1-electron isoelectronic series.

n	l	m	$d\sigma_{nlm}/d\Omega$
2	0	0	$\dfrac{128k'Z^8}{k[q^2 + (3Z/2)^2]^6}$
2	1	0	$\dfrac{288k'Z^{10}\cos^2(\theta_q)}{kq^2[q^2 + (3Z/2)^2]^6}$
2	1	±1	$\dfrac{144k'Z^{10}\sin^2(\theta_q)}{kq^2[q^2 + (3Z/2)^2]^6}$
3	0	0	$\dfrac{1024k'Z^8(3q^2 + (4Z/3)^2)^2}{243k[q^2 + (4Z/3)^2]^8}$
3	1	0	$\dfrac{8192k'Z^{10}(3q^2 + (4Z/3)^2)^2\cos^2(\theta_q)}{729kq^2[q^2 + (4Z/3)^2]^8}$
3	1	±1	$\dfrac{4096k'Z^{10}(3q^2 + (4Z/3)^2)^2\sin^2(\theta_q)}{729kq^2[q^2 + (4Z/3)^2]^8}$
3	2	0	$\dfrac{32768k'Z^{12}[1 + 3\cos(2\theta_q)]^2}{19683k[q^2 + (4Z/3)^2]^8}$
3	2	±1	$\dfrac{6552k'Z^{12}\sin^2(2\theta_q)}{6561k[q^2 + (4Z/3)^2]^8}$
3	2	±2	$\dfrac{6552k'Z^{12}\sin^4(\theta_q)}{6561k[q^2 + (4Z/3)^2]^8}$

Acknowledgements

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