

Many-particle Sturmians

John Avery

H.C. Ørsted Institute, University of Copenhagen, DK-2100 Copenhagen, Denmark

Received 13 January 1997; revised 28 April 1997

The weighted orthonormality relations for many-particle Sturmian basis functions are derived both in momentum space and in position space. It is shown that when these functions are used as a basis, the kinetic energy term disappears from the Schrödinger equation. A general method is developed for constructing many-electron Sturmian basis sets from one-electron Sturmians. This method is illustrated by applications to atoms and ions and to the H_2 molecule. It is shown that the direct solution of the Schrödinger equation using many-particle Sturmian basis functions offers a useful alternative to the Hartree–Fock approximation and configuration interaction; and it is shown that the Sturmian method leads to an automatic optimization of the orbital exponents.

1. Introduction

Sturmian basis functions are solutions for the Schrödinger equation for some easily-solved potential, $V_0(\mathbf{x})$, where the potential is weighted by a factor, β_ν , especially chosen in such a way as to make all of the basis functions in the set correspond to the same energy, regardless of their quantum numbers. Schull and Löwdin [24], who introduced single-electron hydrogenlike Sturmian basis functions into quantum chemistry, did so because these functions are complete without the inclusion of the continuum. The name “Sturmian” was introduced by Rotenberg [23] in order to emphasize the connection with Sturm–Liouville theory. Weniger [26] has studied the orthonormality and completeness properties of Sturmian basis sets and shown that such a set forms the basis of a Sobolev space. The present paper will discuss the many-particle generalization of Sturmian basis sets [9]. We shall make use of the momentum-space representations of these functions, as well as their position-space representations; and therefore we begin by writing the many-particle the Schrödinger equation in momentum space in terms of the mass-weighted coordinates of an N -particle system.

2. The momentum-space Schrödinger equation

Let $e^{i\mathbf{p}\cdot\mathbf{x}}$ be a d -dimensional plane wave defined by

$$e^{i\mathbf{p}\cdot\mathbf{x}} \equiv e^{i(p_1x_1+\dots+p_dx_d)}, \quad (1)$$

where x_1, \dots, x_d are the $d = 3N$ mass-weighted Cartesian coordinates of the particles in an N -particle system. Then we can write

$$\begin{aligned}\psi(\mathbf{x}) &= \frac{1}{(2\pi)^{d/2}} \int d\mathbf{p} e^{i\mathbf{p}\cdot\mathbf{x}} \psi^t(\mathbf{p}), \\ \psi^t(\mathbf{p}) &= \frac{1}{(2\pi)^{d/2}} \int d\mathbf{x} e^{-i\mathbf{p}\cdot\mathbf{x}} \psi(\mathbf{x}),\end{aligned}\quad (2)$$

where

$$\begin{aligned}\psi(\mathbf{x}) &\equiv \psi(x_1, \dots, x_d), \\ \psi^t(\mathbf{p}) &\equiv \psi^t(p_1, \dots, p_d), \\ d\mathbf{x} &\equiv dx_1 dx_2 \dots dx_d, \\ d\mathbf{p} &\equiv dp_1 dp_2 \dots dp_d.\end{aligned}\quad (3)$$

If atomic units are used, the position-space Schrödinger equation can be written in the form

$$[-\Delta + p_0^2 + 2V(\mathbf{x})] \psi(\mathbf{x}) = 0, \quad (4)$$

where

$$p_0^2 \equiv -2E \quad (5)$$

and where Δ is the generalized Laplacian operator

$$\Delta \equiv \sum_{j=1}^d \frac{\partial^2}{\partial x_j^2}. \quad (6)$$

Substituting (2) into (4), we obtain

$$\int d\mathbf{p} e^{i\mathbf{p}\cdot\mathbf{x}} [p^2 + p_0^2 + 2V(\mathbf{x})] \psi^t(\mathbf{p}) = 0. \quad (7)$$

If we now multiply (7) by $e^{-i\mathbf{p}'\cdot\mathbf{x}}$ and integrate over the particle coordinates, we have

$$\begin{aligned}(2\pi)^d \int d\mathbf{p} \delta(\mathbf{p} - \mathbf{p}') (p^2 + p_0^2) \psi^t(\mathbf{p}) \\ + 2 \int d\mathbf{p} \int d\mathbf{x} e^{i(\mathbf{p}-\mathbf{p}')\cdot\mathbf{x}} V(\mathbf{x}) \psi^t(\mathbf{p}) = 0,\end{aligned}\quad (8)$$

which can be rewritten in the form

$$(p'^2 + p_0^2) \psi^t(\mathbf{p}') = -\frac{2}{(2\pi)^{d/2}} \int d\mathbf{p} V^t(\mathbf{p}' - \mathbf{p}) \psi^t(\mathbf{p}), \quad (9)$$

where

$$V^t(\mathbf{p}) \equiv \frac{1}{(2\pi)^{d/2}} \int d\mathbf{x} e^{-i\mathbf{p}\cdot\mathbf{x}} V(\mathbf{x}). \quad (10)$$

Equation (9) is the momentum-space form of the Schrödinger equation.

3. Sturmian basis functions

Suppose that we have two solutions of the position-space Schrödinger equation for some potential, $V_0(\mathbf{x})$, so that

$$\begin{aligned} [\Delta - p_0^2] \phi_\nu(\mathbf{x}) &= 2\beta_\nu V_0(\mathbf{x})\phi_\nu(\mathbf{x}), \\ [\Delta - p_0^2] \phi_{\nu'}^*(\mathbf{x}) &= 2\beta_{\nu'}^* V_0(\mathbf{x})\phi_{\nu'}^*(\mathbf{x}), \end{aligned} \quad (11)$$

where ν stands for a set of quantum numbers labeling the solutions to (11). Here β_ν is a weighting factor, chosen in such a way that both solutions correspond to the same value of p_0 and hence the same energy, although their quantum numbers may be different. If we multiply the two equations respectively by $\phi_{\nu'}^*(\mathbf{x})$ and $\phi_\nu(\mathbf{x})$, integrate over the coordinates, take the difference between the two equations, and make use of the Hermiticity of the operator $\Delta - p_0^2$, we obtain [18]

$$0 = (\beta_{\nu'}^* - \beta_\nu) \int d\mathbf{x} \phi_{\nu'}^*(\mathbf{x}) V_0(\mathbf{x}) \phi_\nu(\mathbf{x}). \quad (12)$$

Thus β_ν must be real, and whenever $\beta_{\nu'} \neq \beta_\nu$, the two Sturmian functions are orthogonal with respect to potential-weighted integration over the coordinates. It is convenient to normalize our Sturmian basis sets in such a way that

$$\int d\mathbf{x} \phi_{\nu'}^*(\mathbf{x}) V_0(\mathbf{x}) \phi_\nu(\mathbf{x}) = -\frac{p_0^2}{\beta_\nu} \delta_{\nu',\nu}. \quad (13)$$

This special normalization is convenient because it leads to momentum-space orthonormality relations of the form

$$\int dp \left(\frac{p_0^2 + p^2}{2p_0^2} \right) \phi_{\nu'}^{*t}(\mathbf{p}) \phi_\nu^t(\mathbf{p}) = \delta_{\nu',\nu} \quad (14)$$

regardless of the dimension of the space. To show that (14) follows from (13) we first use the d -dimensional Fourier convolution theorem to rewrite the momentum-space Schrödinger equation (9) in the form

$$(p_0^2 + p^2) \psi^t(\mathbf{p}) = -\frac{2}{(2\pi)^{d/2}} \int d\mathbf{x} e^{i\mathbf{p}\cdot\mathbf{x}} V(\mathbf{x}) \psi(\mathbf{x}). \quad (15)$$

The Sturmian basis functions $\phi_\nu(\mathbf{x})$ and their Fourier transforms $\phi_\nu^t(\mathbf{p})$ will thus be solutions of

$$(p_0^2 + p^2) \phi_\nu^t(\mathbf{p}) = -\frac{2\beta_\nu}{(2\pi)^{d/2}} \int d\mathbf{x} e^{i\mathbf{p}\cdot\mathbf{x}} V_0(\mathbf{x}) \phi_\nu(\mathbf{x}) \quad (16)$$

so that

$$[V_0(\mathbf{x}) \phi_\nu(\mathbf{x})]^t = -\frac{1}{2\beta_\nu} (p_0^2 + p^2) \phi_\nu^t(\mathbf{p}). \quad (17)$$

We also know that the scalar product of two functions in position space is equal to the scalar product of their Fourier transforms in momentum space, so that

$$\begin{aligned}
 -\frac{p_0^2}{\beta_\nu} \delta_{\nu',\nu} &= \int d\mathbf{x} \phi_{\nu'}^*(\mathbf{x}) V_0(\mathbf{x}) \phi_\nu(\mathbf{x}) \\
 &= \int d\mathbf{p} [\phi_{\nu'}^*(\mathbf{x})]^t [V_0(\mathbf{x}) \phi_\nu(\mathbf{x})]^t \\
 &= - \int d\mathbf{p} \phi_{\nu'}^{t*}(\mathbf{p}) \frac{(p_0^2 + p^2)}{2\beta_\nu} \phi_\nu^t(\mathbf{p}). \tag{18}
 \end{aligned}$$

Multiplying (18) by $-\beta_\nu/p_0^2$, we obtain (14). The meaning of the orthonormality relations, (13) and (14), requires a further comment: Since we are dealing with a many-dimensional space, ν represents a set of quantum numbers rather than a single quantum number. Orthogonality with respect to the quantum number (or numbers) on which β_ν depends (the ‘‘grand principal quantum number(s)’’) follows automatically from (12), i.e., Sturmian basis functions corresponding to different values of β_ν are necessarily orthogonal; but orthogonality with respect to the minor quantum numbers must be constructed or proved in some other way, for example by symmetry arguments.

4. Sturmian expansion of a plane wave; Elimination of the kinetic energy

The expansion of a plane wave in terms of single-particle hydrogenlike Sturmian basis functions and their Fourier transforms was first derived by Shibuya and Wulfman [25,26]. Later Aquilanti and his co-workers generalized this expansion to many-particle Sturmians [1,2]. The derivation of the d -dimensional expansion, which makes use of the weighted momentum-space orthonormality relation, is as follows: If we let

$$e^{i\mathbf{p}\cdot\mathbf{x}} = \left(\frac{p_0^2 + p^2}{2p_0^2} \right) \sum_{\nu'} \phi_{\nu'}^t(\mathbf{p}) a_{\nu'}(\mathbf{x}) \tag{19}$$

then the coefficients in the expansion, $a_{\nu'}(\mathbf{x})$, can be determined by multiplying on the left by $\phi_\nu^{t*}(\mathbf{p})$ and integrating over $d\mathbf{p}$. This yields

$$a_\nu(\mathbf{x}) = \int d\mathbf{p} e^{i\mathbf{p}\cdot\mathbf{x}} \phi_\nu^{t*}(\mathbf{p}) = (2\pi)^{d/2} \phi_\nu^*(\mathbf{x}) \tag{20}$$

so that

$$e^{i\mathbf{p}\cdot\mathbf{x}} = (2\pi)^{d/2} \left(\frac{p_0^2 + p^2}{2p_0^2} \right) \sum_\nu \phi_\nu^t(\mathbf{p}) \phi_\nu^*(\mathbf{x}). \tag{21}$$

If we substitute this expansion into (15) and cancel $p_0^2 + p^2$ from both sides, we obtain a form of the Schrödinger equation in which the the kinetic energy term has disappeared:

$$\psi^t(\mathbf{p}) = -\frac{1}{p_0^2} \sum_\nu \phi_\nu^t(\mathbf{p}) \int d\mathbf{x} \phi_\nu^*(\mathbf{x}) V(\mathbf{x}) \psi(\mathbf{x}),$$

$$\psi(\mathbf{x}) = -\frac{1}{p_0^2} \sum_{\nu} \phi_{\nu}(\mathbf{x}) \int dx' \phi_{\nu}^*(\mathbf{x}') V(\mathbf{x}') \psi(\mathbf{x}'). \quad (22)$$

If the wave function is expanded in terms of the Sturmian basis functions, so that $\psi(\mathbf{x}) = \sum_{\nu} \phi_{\nu}(\mathbf{x}) B_{\nu}$, then, substituting the expansion into (22), we find that the expansion coefficients and p_0 must satisfy the secular equation

$$\sum_{\nu} [T_{\nu',\nu} - p_0 \delta_{\nu',\nu}] B_{\nu} = 0, \quad (23)$$

where

$$T_{\nu',\nu} \equiv -\frac{1}{p_0} \int dx \phi_{\nu'}^*(\mathbf{x}) V(\mathbf{x}) \phi_{\nu}(\mathbf{x}). \quad (24)$$

For systems interacting through Coulomb forces, $T_{\nu',\nu}$ is independent of p_0 . Notice that the eigenvalues of the Sturmian secular equation (23) are not values of the energy but values of the parameter p_0 , which is related to the binding energy of bound states by equation (5). The Sturmian secular equation (23), from which the kinetic energy term has vanished, can be derived on another way: If we begin with the position-space Schrödinger equation and expand the wave function in terms of a set of solutions of equation (11), we obtain

$$\sum_{\nu} [-\Delta + p_0^2 + 2V(\mathbf{x})] \phi_{\nu}(\mathbf{x}) B_{\nu} = 0. \quad (25)$$

Since the Sturmian basis functions, $\phi_{\nu}(\mathbf{x})$, are solutions of (11), equation (25) can be rewritten in the form

$$\sum_{\nu} [-\beta_{\nu} V_0(\mathbf{x}) + V(\mathbf{x})] \phi_{\nu}(\mathbf{x}) B_{\nu} = 0, \quad (26)$$

we now multiply (26) on the left by $\phi_{\nu'}^*(\mathbf{x})$ and integrate over the coordinates, making use of the orthonormality relation shown in equation (13):

$$\sum_{\nu} \left[p_0^2 \delta_{\nu',\nu} + \int dx \phi_{\nu'}^*(\mathbf{x}) V(\mathbf{x}) \phi_{\nu}(\mathbf{x}) \right] B_{\nu} = 0. \quad (27)$$

With the definition of $T_{\nu',\nu}$ given in (24), equation (27) reduces to the Sturmian secular equation (23).

5. Construction of many-electron Sturmians

If we let \mathbf{x}_j represent the Cartesian coordinates of the j th electron in an N -electron system, and if $V_0(\mathbf{x})$ is an external potential, then

$$V_0(\mathbf{x}) = \sum_{j=1}^N v(\mathbf{x}_j), \quad (28)$$

where $v(\mathbf{x}_j)$ is the potential experienced by a single electron. Suppose that we know a set of functions, $\chi_\mu(\mathbf{x})$ which satisfy one-electron equations of the form

$$[\Delta_j - k_\mu^2] \chi_\mu(\mathbf{x}_j) = 2b_\mu k_\mu v(\mathbf{x}_j) \chi_\mu(\mathbf{x}_j), \quad (29)$$

where

$$\Delta_j \equiv \frac{\partial^2}{\partial x_j^2} + \frac{\partial^2}{\partial y_j^2} + \frac{\partial^2}{\partial z_j^2} \quad (30)$$

so that

$$\sum_{j=1}^N \Delta_j = \Delta, \quad (31)$$

and let us suppose that the parameters k_μ and b_μ are chosen in such a way that

$$k_\mu^2 + k_{\mu'}^2 + k_{\mu''}^2 + \cdots = p_0^2 \quad (32)$$

and

$$k_\mu b_\mu = \beta_\nu. \quad (33)$$

Then

$$\phi_\nu(\mathbf{x}) = \chi_\mu(\mathbf{x}_1) \chi_{\mu'}(\mathbf{x}_2) \cdots \chi_{\mu''}(\mathbf{x}_N) \quad (34)$$

will satisfy

$$[\Delta - p_0^2] \phi_\nu(\mathbf{x}) = 2\beta_\nu V_0(\mathbf{x}) \phi_\nu(\mathbf{x}) \quad (35)$$

with

$$p_0^2 = \beta_\nu^2 \left(\frac{1}{b_\mu^2} + \frac{1}{b_{\mu'}^2} + \frac{1}{b_{\mu''}^2} + \cdots \right) \quad (36)$$

or, expressed in a different way,

$$\beta_\nu = p_0 \left(\frac{1}{b_\mu^2} + \frac{1}{b_{\mu'}^2} + \frac{1}{b_{\mu''}^2} + \cdots \right)^{-1/2} \quad (37)$$

and

$$k_\mu = \frac{p_0}{b_\mu} \left(\frac{1}{b_\mu^2} + \frac{1}{b_{\mu'}^2} + \frac{1}{b_{\mu''}^2} + \cdots \right)^{-1/2}. \quad (38)$$

This gives us a prescription for constructing many-electron Sturmians provided we are able to solve the single-electron Schrödinger equation (29), and provided that the parameters k_μ and b_μ satisfy the subsidiary relations (32) and (33). Antisymmetrized products of functions of the form shown in equation (34) will, of course, also satisfy (35).

6. *N*-electron atoms

As an illustrative example, we can consider the ground states and excited states of *N*-electron atoms in the approximation where the nucleus is assumed to be infinitely heavy. In this example,

$$v(\mathbf{x}_j) = -\frac{Z}{r_j}, \tag{39}$$

where *Z* is the nuclear charge, and where *r_j* is the distances the *j*th electron from the nucleus. We next let

$$\begin{aligned} \chi_{nlm,+1/2}(\mathbf{x}_j) &= R_{nl}(r_j)Y_{lm}(\theta_j, \phi_j)\alpha(j), \\ \chi_{nlm,-1/2}(\mathbf{x}_j) &= R_{nl}(r_j)Y_{lm}(\theta_j, \phi_j)\beta(j), \end{aligned} \tag{40}$$

where

$$\begin{aligned} R_{nl}(r_j) &= \mathcal{N}_{nl}(2k_n r_j)^l e^{-k_n r_j} F(l+1-n|2l+2|2k_n r_j), \\ \mathcal{N}_{nl} &= \frac{2k_n^{3/2}}{(2l+1)!} \sqrt{\frac{(l+n)!}{n(n-l-1)!}}, \end{aligned} \tag{41}$$

and where *F(a|b|c)* is a confluent hypergeometric function. The functions $\chi_{nlms}(\mathbf{x}_j)$ are one-electron hydrogenlike Sturmians, and they can be shown to obey the following equations:

$$[\Delta_j - k_n^2] \chi_{nlms}(\mathbf{x}_j) = 2 \left(\frac{nk_n}{Z} \right) \left(-\frac{Z}{r_j} \right) \chi_{nlms}(\mathbf{x}_j), \tag{42}$$

$$\int d\tau_j |\chi_{nlms}(\mathbf{x}_j)|^2 \left(-\frac{Z}{r_j} \right) = -\frac{k_n^2}{(nk_n/Z)} \tag{43}$$

and

$$\int d\tau_j |\chi_{nlms}(\mathbf{x}_j)|^2 = 1, \tag{44}$$

where $\int d\tau_j$ stands for integration over the space coordinates and summation over the spin coordinates of the *j*th electron. Within the set of one-electron hydrogenlike Sturmians corresponding to a particular value of β_ν , an additional orthonormality relation holds:

$$\int d\tau_j \chi_{nlms}^*(\mathbf{x}_j) \chi_{n'l'm's'}(\mathbf{x}_j) = \delta_{n'n} \delta_{l'l} \delta_{m'm} \delta_{s's}. \tag{45}$$

Then

$$\phi_\nu(\mathbf{x}) \equiv \chi_{nlms}(\mathbf{x}_1) \chi_{n'l'm's'}(\mathbf{x}_2) \cdots \chi_{n''l''m''s''}(\mathbf{x}_N) \tag{46}$$

will satisfy equation (35), provided that

$$\beta_\nu = \frac{nk_n}{Z} = \frac{n'k_{n'}}{Z} = \dots \quad (47)$$

and

$$p_0^2 = k_n^2 + k_{n'}^2 + \dots, \quad (48)$$

where $V_0(\mathbf{x})$ is defined by equation (28). Equations (47) and (48) can be combined to yield

$$\beta_\nu = \frac{p_0}{Z} \left(\frac{1}{n^2} + \frac{1}{n'^2} + \dots \right)^{-1/2} \quad (49)$$

and

$$k_n = \frac{Z\beta_\nu}{n} = \frac{p_0}{n} \left(\frac{1}{n^2} + \frac{1}{n'^2} + \dots \right)^{-1/2}. \quad (50)$$

In the lowest approximation, we can represent the ground-state of an atom or ion by a single determinantal Sturmian function. For example, the 1S ground states of the two-electron isoelectronic series can be represented in the lowest approximation by the single determinantal Sturmian basis function:

$$\phi_0(\mathbf{x}) = |\chi_{1s}\chi_{\bar{1}s}| \equiv \frac{1}{\sqrt{2}} [\chi_{1s}(1)\chi_{\bar{1}s}(2) - \chi_{1s}(2)\chi_{\bar{1}s}(1)]. \quad (51)$$

Similarly, the 2S ground states of the three-electron isoelectronic series can be approximates by

$$\phi_0(\mathbf{x}) = |\chi_{1s}\chi_{\bar{1}s}\chi_{2s}| \quad (52)$$

and the 1S ground states of the four-electron isoelectronic series by

$$\phi_0(\mathbf{x}) = |\chi_{1s}\chi_{\bar{1}s}\chi_{2s}\chi_{\bar{2}s}|. \quad (53)$$

The determinantal wave functions shown in equations (51)–(53) have the correct normalization for many-electron Sturmians (i.e., the normalization required by equation (13)). To see this, we can make use of the Slater–Condon rules, which hold for the diagonal matrix elements of

$$V_0(\mathbf{x}) = - \sum_{j=1}^N \frac{Z}{r_j} \quad (54)$$

because of equation (45). From the Slater–Condon rules, and from equations (42)–(45), (51)–(53) and (54), it follows that

$$-\frac{1}{p_0} \int dx |\phi_0(\mathbf{x})|^2 V_0(\mathbf{x}) = - \sum_{\mu} \frac{1}{p_0} \int d\tau_1 |\chi_{\mu}(1)|^2 \left(-\frac{Z}{r_1} \right) = \frac{1}{p_0} \sum_n \frac{k_n^2}{(nk_n/Z)}$$

$$= \frac{p_0}{\beta_0} = Z \left(\frac{1}{n^2} + \frac{1}{n'^2} + \dots \right)^{1/2}. \quad (55)$$

In our example,

$$V(\mathbf{x}) = V_0(\mathbf{x}) + V'(\mathbf{x}), \quad (56)$$

where $V'(\mathbf{x})$ is the interelectron repulsion term:

$$V'(\mathbf{x}) = \sum_{i>j}^N \sum_{j=1}^N \frac{1}{r_{ij}}. \quad (57)$$

Again making use of the Slater–Condon rules, we find that

$$\begin{aligned} -\frac{1}{p_0} \int d\mathbf{x} |\phi_0(\mathbf{x})|^2 V'(\mathbf{x}) &= -\frac{1}{p_0} \sum_{\mu'>\mu} \sum_{\mu} \int d\tau_1 \int d\tau_2 [|\chi_{\mu}(1)|^2 |\chi_{\mu'}(2)|^2 \\ &\quad - \chi_{\mu}^*(1) \chi_{\mu'}(1) \chi_{\mu}(2) \chi_{\mu'}^*(2)] \frac{1}{r_{12}} \equiv T'_{0,0}. \end{aligned} \quad (58)$$

For the isoelectronic series of atoms and ions whose wave functions can be represented in a crude approximation by the many-electron Sturmians shown in equations (51)–(53), the interelectron repulsion term becomes, respectively, for the 2-electron series:

$$T'_{0,0} = -\frac{1}{p_0(4\pi)^2} \int d^3x_1 \int d^3x_2 \frac{1}{r_{12}} |R_{10}(r_1)|^2 |R_{10}(r_2)|^2, \quad (59)$$

for the 3-electron series:

$$\begin{aligned} T'_{0,0} &= -\frac{1}{p_0(4\pi)^2} \int d^3x_1 \int d^3x_2 \frac{1}{r_{12}} [|R_{10}(r_1)|^2 |R_{10}(r_2)|^2 \\ &\quad + 2 |R_{10}(r_1)|^2 |R_{20}(r_2)|^2 - R_{10}(r_1) R_{20}(r_1) R_{10}(r_2) R_{20}(r_2)], \end{aligned} \quad (60)$$

and for the 4-electron series:

$$\begin{aligned} T'_{0,0} &= -\frac{1}{p_0(4\pi)^2} \int d^3x_1 \int d^3x_2 \frac{1}{r_{12}} [|R_{10}(r_1)|^2 |R_{10}(r_2)|^2 \\ &\quad + 4 |R_{10}(r_1)|^2 |R_{20}(r_2)|^2 + |R_{20}(r_1)|^2 |R_{20}(r_2)|^2 \\ &\quad - 2 R_{10}(r_1) R_{20}(r_1) R_{10}(r_2) R_{20}(r_2)]. \end{aligned} \quad (61)$$

The interelectron repulsion integrals in equations (59)–(61) can be evaluated by means of the relationship

$$\frac{1}{r_{12}} = \frac{1}{2\pi^2} \int \frac{d^3k}{k^2} e^{i\mathbf{k}\cdot(\mathbf{x}_1 - \mathbf{x}_2)}, \quad (62)$$

from which we obtain (for example)

$$\begin{aligned} & \frac{1}{(4\pi)^2} \int d^3x_1 \int d^3x_2 \frac{1}{r_{12}} |R_{10}(r_1)|^2 |R_{10}(r_2)|^2 \\ &= \frac{1}{2\pi^2(4\pi)^2} \int \frac{d^3k}{k^2} \int d^3x_1 e^{i\mathbf{k}\cdot\mathbf{x}_1} |R_{10}(r_1)|^2 \int d^3x_2 e^{-i\mathbf{k}\cdot\mathbf{x}_2} |R_{10}(r_2)|^2. \end{aligned} \quad (63)$$

Expanding the plane waves in terms of spherical harmonics and spherical Bessel functions, we obtain

$$\begin{aligned} \frac{1}{4\pi} \int d^3x_1 e^{i\mathbf{k}\cdot\mathbf{x}_1} |R_{10}(r_1)|^2 &= \int_0^\infty dr_1 r_1^2 |R_{10}(r_1)|^2 j_0(kr_1) \\ &= 4k_1^3 \int_0^\infty dr_1 r_1^2 e^{-2k_1 r_1} j_0(kr_1) \\ &= \frac{16k_1^4}{(k^2 + 4k_1^2)^2} \end{aligned} \quad (64)$$

and, similarly,

$$\frac{1}{4\pi} \int d^3x_2 e^{-i\mathbf{k}\cdot\mathbf{x}_2} |R_{10}(r_2)|^2 = \frac{16k_1^4}{(k^2 + 4k_1^2)^2}. \quad (65)$$

In equations (64) and (65), we have made use of the properties of spherical Bessel functions, studied by Geller et al. [17,19]. These authors derived recursion relations for integrals of the form

$$J_{jl}(k, \zeta) \equiv \int_0^\infty dr r^j e^{-\zeta r} j_l(kr). \quad (66)$$

The most simple of these integrals is

$$J_{10}(k, \zeta) \equiv \int_0^\infty dr r e^{-\zeta r} j_0(kr) = \frac{1}{k} \int_0^\infty dr e^{-\zeta r} \sin(kr), \quad (67)$$

which can be evaluated by elementary integration, yielding

$$J_{1,0}(k, \zeta) = \frac{1}{k^2 + \zeta^2}. \quad (68)$$

The other integrals can be derived from $J_{1,0}$ by means of the recursion relations

$$J_{l+1,l}(k, \zeta) = \frac{2lk}{k^2 + \zeta^2} J_{l,l-1}(k, \zeta) \quad (69)$$

and

$$J_{j+1,l}(k, \zeta) = -\frac{\partial}{\partial \zeta} J_{j,l}(k, \zeta). \quad (70)$$

Thus, for example, we find that

$$J_{2,0}(k, \zeta) = \frac{2\zeta}{(k^2 + \zeta^2)^2}, \tag{71}$$

$$J_{3,0}(k, \zeta) = \frac{2(3\zeta^2 - k^2)}{(k^2 + \zeta^2)^3}, \tag{72}$$

$$J_{2,1}(k, \zeta) = \frac{2k}{(k^2 + \zeta^2)^2}, \tag{73}$$

$$J_{3,1}(k, \zeta) = \frac{8k\zeta}{(k^2 + \zeta^2)^3}, \tag{74}$$

and so on. Combining equations (63)–(65) and integrating over $d\Omega_k$, we obtain

$$\frac{1}{(4\pi)^2} \int d^3x_1 \int d^3x_2 \frac{1}{r_{12}} |R_{10}(r_1)|^2 |R_{10}(r_2)|^2 = \frac{2}{\pi} \int_0^\infty dk \left(\frac{4k_1^2}{k^2 + 4k_1^2} \right)^4. \tag{75}$$

Since the integrand on the right-hand side of equation (75) is an even function of k , we can divide by 2 and let the integral run from $-\infty$ to $+\infty$. If we close the contour in the upper half of the complex k -plane, then Cauchy's integral theorem tells us that the value of the integral is $2\pi i$ times the sum of the residues at the singular points within the contour. In the case of equation (75) the only singularity within the contour is a 4th-order pole at $k = 2ik_1$; and we obtain, with the help of Mathematica,

$$\frac{1}{(4\pi)^2} \int d^3x_1 \int d^3x_2 \frac{1}{r_{12}} |R_{10}(r_1)|^2 |R_{10}(r_2)|^2 = \frac{5}{8} k_1 \tag{76}$$

and, similarly,

$$\frac{1}{(4\pi)^2} \int d^3x_1 \int d^3x_2 \frac{1}{r_{12}} |R_{20}(r_1)|^2 |R_{20}(r_2)|^2 = \frac{77}{256} k_2, \tag{77}$$

$$\frac{1}{(4\pi)^2} \int d^3x_1 \int d^3x_2 \frac{1}{r_{12}} |R_{10}(r_1)|^2 |R_{20}(r_2)|^2 = \frac{34}{81} k_2, \tag{78}$$

$$\frac{1}{(4\pi)^2} \int d^3x_1 \int d^3x_2 \frac{1}{r_{12}} R_{10}(r_1) R_{20}(r_1) R_{10}(r_2) R_{20}(r_2) = \frac{32}{729} k_2, \tag{79}$$

where we have made use of the fact that, from equation (50), $k_1 = 2k_2$. The integrals shown in equations (55), (59)–(61) and (76)–(79) are the ones which we need to solve the Sturmian secular equations for the 2-electron, 3-electron and 4-electron isoelectronic series of atoms and ions in the crudest approximation. Substituting the integrals into equation (23) (where the summation disappears because only a single basis function is used), we obtain, respectively, for the 2-electron series:

$$p_0 = \sqrt{2} \left[Z - \left(\frac{1}{2} \right) \left(\frac{5}{8} \right) \right], \tag{80}$$

for the 3-electron series:

$$p_0 = \frac{3}{2}Z - \left(\frac{2}{3}\right) \left(\frac{5}{8}\right) - \left(\frac{2}{3}\right) \left(\frac{34}{81}\right) + \left(\frac{1}{3}\right) \left(\frac{32}{729}\right), \quad (81)$$

and for the 4-electron series:

$$p_0 = \sqrt{\frac{5}{2}} \left[Z - \left(\frac{2}{5}\right) \left(\frac{5}{8}\right) - \left(\frac{1}{5}\right) \left(\frac{77}{256}\right) - \left(\frac{4}{5}\right) \left(\frac{34}{81}\right) + \left(\frac{2}{5}\right) \left(\frac{32}{729}\right) \right]. \quad (82)$$

Figure 1 shows the Clementi's values for the ground state energies of the 3-electron isoelectronic series (points) compared with a smooth curve showing the energies derived from equation (81) through the relationship $E = -p_0^2/2$, while figure 2 shows a similar comparison for the 4-electron series. Since, as can be seen from the figures, even the crudest representation of the wave function as a single many-electron Sturmian gives reasonably accurate results, it is interesting to ask whether better accuracy can be achieved by using a larger set of many-electron Sturmians. As has been pointed out by Aquilanti and Avery [1], generalized potential harmonics (analogous to the potential harmonics introduced into nuclear physics by Fabre de la Ripelle [10,12–14]), can be constructed from many-particle Sturmians in the following way: The Schrödinger equation in the form shown in equation (22) can be iterated starting with some zeroth-order trial function. For the three isoelectronic series which we are using as examples, it is appropriate to let the zeroth-order wave functions be the ones shown in equations (51)–(53). If we let $\psi_1(\mathbf{x})$ represent the first-iterated wave function, and if we make explicit the fact that ν is not a single quantum number, but a set of quantum numbers, we obtain

$$\begin{aligned} \psi_1(\mathbf{x}) &= -\frac{1}{p_0^2} \sum_{\nu_1, \nu_2, \dots} \phi_{\nu_1, \nu_2, \dots}(\mathbf{x}) \int dx' \phi_{\nu_1, \nu_2, \dots}^*(\mathbf{x}') V(\mathbf{x}') \phi_0(\mathbf{x}') \\ &= -\frac{1}{p_0^2} \sum_{\nu_1} f_{\nu_1}(\mathbf{x}), \end{aligned} \quad (83)$$

where

$$f_{\nu_1}(\mathbf{x}) \equiv \sum_{\nu_2, \dots} \phi_{\nu_1, \nu_2, \dots}(\mathbf{x}) \int dx' \phi_{\nu_1, \nu_2, \dots}^*(\mathbf{x}') V(\mathbf{x}') \phi_0(\mathbf{x}'). \quad (84)$$

If we let ν_1 stand for the the quantum number (or numbers) on which β_ν depends while ν_2, ν_3, \dots stand for the minor quantum numbers, then, apart from a normalization constant, the functions $f_{\nu_1}(\mathbf{x})$ shown in equation (84) are the generalized potential harmonics of Aquilanti and Avery. Clearly they contribute importantly to the true wave function, since the first-iterated wave function can be expressed entirely in terms of them. The energies of a series of simple atoms and ions were calculated by Aquilanti and Avery [1] using a basis set of only four generalized potential harmonics. The energy values calculated by Aquilanti and Avery represent a considerable improvement over the Hartree–Fock limit [11], roughly half the correlation energy being recovered, and it seems likely that higher accuracy could be achieved by using a larger number of potential harmonics.

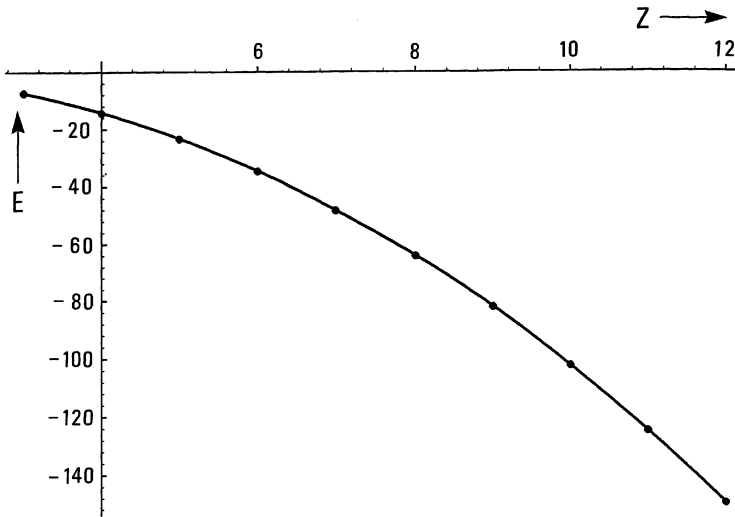


Figure 1. Ground-state energies in Hartrees for ions and atoms in the 3-electron series, Li, Be⁺, B²⁺, C³⁺, N⁴⁺, O⁵⁺, F⁶⁺, Ne⁷⁺, Na⁸⁺, and Mg⁹⁺, calculated from equation (81) through the relationship $E = -p_0^2/2$, compared with Clementi's values (dots, [11]).

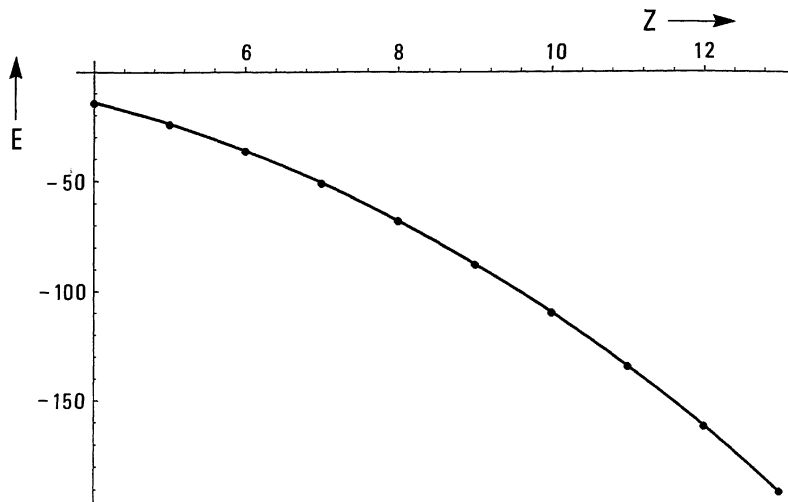


Figure 2. Ground-state energies for the 4-electron series, Be, B⁺, C²⁺, etc., calculated from equation (82) (smooth curve), compared with Clementi's values (dots, [11]).

7. Many-electron Sturmians for molecules

If we wish to apply the formalism outlined in equations (23) and (28)–(38) to molecules, then we can let $V_0(\mathbf{x})$ be the nuclear attraction potential produced by nuclei with positive charges Z_a located at the points \mathbf{X}_a , while, as before, $V'(\mathbf{x})$ will be the interelectron repulsion potential. Then the potential experienced by a single electron

will then be

$$v(\mathbf{x}_j) = - \sum_a \frac{Z_a}{|\mathbf{x}_j - \mathbf{X}_a|}. \quad (85)$$

Momentum-space methods, pioneered by Fock, Shibuya, Wulfman, Judd, Koga, Aquilanti and others [3–8,15,16,20–22], provide us with an elegant method for solving the one-electron equation

$$[\Delta_j - k_\mu^2] \varphi_\mu(\mathbf{x}_j) = 2b_\mu k_\mu v(\mathbf{x}_j) \varphi_\mu(\mathbf{x}_j), \quad (86)$$

where $v(\mathbf{x}_j)$ is the single-electron nuclear attraction potential shown in equation (85). To obtain these solutions, we let

$$\varphi_\mu^t(\mathbf{p}) \equiv \frac{1}{(2\pi)^{3/2}} \int d^3x_j e^{-i\mathbf{p}\cdot\mathbf{x}_j} \varphi_\mu(\mathbf{x}_j) \quad (87)$$

and

$$\chi_{nlm}^t(\mathbf{p}) \equiv \frac{1}{(2\pi)^{3/2}} \int d^3x_j e^{-i\mathbf{p}\cdot\mathbf{x}_j} R_{nl}(r_j) Y_{lm}(\hat{\mathbf{x}}_j), \quad (88)$$

where the functions $R_{nl}(r_j)$ are the hydrogenlike Sturmian wave functions defined by equation (41) with $k_n = k_\mu$ for all the functions in the set. From equations (9) and (42), and from the relationship

$$\left[\frac{1}{r_j} \right]^t \equiv \frac{1}{(2\pi)^{3/2}} \int d^3x_j e^{-i\mathbf{p}\cdot\mathbf{x}_j} \frac{1}{r_j} = \sqrt{\frac{2}{\pi}} \frac{1}{p^2} \quad (89)$$

it follows that the Fourier-transformed hydrogenlike Sturmians obey the integral equation

$$(p^2 + k_\mu^2) \chi_{nlm}^t(\mathbf{p}) = \frac{nk_\mu}{\pi^2} \int d^3p' \frac{1}{|\mathbf{p} - \mathbf{p}'|^2} \chi_{nlm}^t(\mathbf{p}'). \quad (90)$$

Remembering the momentum-space orthonormality relations (14), from which it follows that

$$\int d^3p' \left(\frac{p'^2 + k_\mu^2}{2k_\mu^2} \right) \chi_{n'l'm'}^{t*}(\mathbf{p}') \chi_{nlm}^t(\mathbf{p}') = \delta_{n'n} \delta_{l'l} \delta_{m'm}, \quad (91)$$

we can see that it is possible to represent the kernel of the integral equation (90) in the form

$$\frac{1}{\pi^2} \frac{1}{|\mathbf{p} - \mathbf{p}'|^2} = \frac{(p^2 + k_\mu^2)(p'^2 + k_\mu^2)}{2k_\mu^2} \sum_{n'l'm'} \frac{1}{n'k_\mu} \chi_{n'l'm'}^t(\mathbf{p}) \chi_{n'l'm'}^{t*}(\mathbf{p}') \quad (92)$$

because, if we substitute the expansion of equation (92) into the right-hand side of (90), we obtain the left-hand side. The Fourier transform of the nuclear attraction potential shown in equation (85) is

$$v^t(\mathbf{p}) = -\sqrt{\frac{2}{\pi}} \sum_a \frac{Z_a}{p^2} e^{i\mathbf{p} \cdot \mathbf{X}_a} \quad (93)$$

so that

$$v^t(\mathbf{p} - \mathbf{p}') = -\sqrt{\frac{2}{\pi}} \sum_a \frac{Z_a}{|\mathbf{p} - \mathbf{p}'|^2} e^{i(\mathbf{p} - \mathbf{p}') \cdot \mathbf{X}_a}. \quad (94)$$

Combining (9), (86), (92) and (94), we obtain

$$\begin{aligned} \varphi_\mu^t(\mathbf{p}) &= b_\mu \sum_{a'n'l'm'} \sqrt{\frac{Z_{a'}}{n'}} e^{i\mathbf{p} \cdot \mathbf{X}_{a'}} \chi_{n'l'm'}^t(\mathbf{p}) \\ &\times \int d^3p' \left(\frac{p'^2 + k_\mu^2}{2k_\mu^2} \right) \sqrt{\frac{Z_{a'}}{n'}} e^{-i\mathbf{p}' \cdot \mathbf{X}_{a'}} \chi_{n'l'm'}^{t*}(\mathbf{p}') \varphi_\mu^t(\mathbf{p}') \end{aligned} \quad (95)$$

or

$$\varphi_\mu^t(\mathbf{p}) = b_\mu \sum_\tau \xi_\tau(\mathbf{p}) \int d^3p' \left(\frac{p'^2 + k_\mu^2}{2k_\mu^2} \right) \xi_\tau^*(\mathbf{p}') \varphi_\mu^t(\mathbf{p}'), \quad (96)$$

where τ stands for the set of indices a, n, l, m , and where

$$\xi_\tau(\mathbf{p}) \equiv \sqrt{\frac{Z_a}{n}} e^{i\mathbf{p} \cdot \mathbf{X}_a} \chi_{nlm}^t(\mathbf{p}). \quad (97)$$

We now let

$$\varphi_\mu^t(\mathbf{p}) = \sum_\tau \xi_\tau(\mathbf{p}) C_{\tau,\mu}. \quad (98)$$

Then (96) will be satisfied provided that

$$\sum_\tau [K_{\tau',\tau} - b_\mu^{-1} \delta_{\tau',\tau}] C_{\tau,\mu} = 0, \quad (99)$$

where

$$K_{\tau',\tau} \equiv \int d^3p \left(\frac{p^2 + k_\mu^2}{2k_\mu^2} \right) \xi_{\tau'}^*(\mathbf{p}) \xi_\tau(\mathbf{p}). \quad (100)$$

The integrals $K_{\tau',\tau}$ for the first few values of n, l and m are shown in table 1. Having found solutions to the one-electron equations (86), we can build up many-electron Sturmians from the spin-up and spin-down functions:

$$\begin{aligned} \varphi_\mu(j) &\equiv \varphi_\mu(\mathbf{x}_j) \alpha(j), \\ \varphi_{\bar{\mu}}(j) &\equiv \varphi_\mu(\mathbf{x}_j) \beta(j). \end{aligned} \quad (101)$$

Table 1

This table shows the first few values of the Shibuya–Wulfman integrals, $S_{\tau',\tau}$, which are related to the integrals defined in equation (100) by $K_{\tau',\tau} = \sqrt{Z_{a'}Z_a/(n'n)}S_{\tau',\tau}$. The vector $\mathbf{s} = (s_1, s_2, s_3)$ is defined by $\mathbf{s} = k_\mu(\mathbf{X}_a - \mathbf{X}_{a'})$, so that $s = k_\mu R$, where R is the internuclear separation.

τ'	$\tau = 1s$	$\tau = 2s$	τ'	$\tau = 2p_1$
$1s$	$(1+s)e^{-s}$	$-2s^2e^{-s}/3$	$2p_1$	$(3+3s+s^2-s_1^2-ss_1^2)e^{-s}/3$
$2s$	$-2s^2e^{-s}/3$	$(3+3s-2s^2+s^3)e^{-s}/3$	$2p_2$	$s_1s_2(1+s)e^{-s}/3$
$2p_j$	$2s_j(1+s)e^{-s}/3$	$s_j(1+s-s^2)e^{-s}/3$	$2p_3$	$s_1s_3(1+s)e^{-s}/3$

For example, the ground state of the hydrogen molecule can be represented in a rough approximation by a basis set consisting of two determinantal Sturmians:

$$\begin{aligned}\phi_1(\mathbf{x}) &= |\varphi_g\varphi_{\bar{g}}| \equiv \varphi_g(\mathbf{x}_1)\varphi_g(\mathbf{x}_2)\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \alpha(2)\beta(1)], \\ \phi_2(\mathbf{x}) &= |\varphi_u\varphi_{\bar{u}}| \equiv \varphi_u(\mathbf{x}_1)\varphi_u(\mathbf{x}_2)\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \alpha(2)\beta(1)],\end{aligned}\quad (102)$$

where g and u denote respectively the $\sigma_g 1s$ *gerade* and the $\sigma_u^* 1s$ *ungerade* solutions to equation (86), with

$$v(\mathbf{x}_j) = -\frac{1}{|\mathbf{x}_j - \mathbf{X}_1|} - \frac{1}{|\mathbf{x}_j - \mathbf{X}_2|}. \quad (103)$$

These one-electron solutions can be found by diagonalizing the matrix $K_{\tau',\tau}$ (equations (97)–(100)), and the one-electron energies thus obtained are shown in figure 3. The Sturmian secular equation (23), then requires that

$$\begin{vmatrix} T_{1,1} - p_0 & T_{1,2} \\ T_{2,1} & T_{2,2} - p_0 \end{vmatrix} = 0, \quad (104)$$

where

$$T_{\nu',\nu} = \frac{p_0}{\beta_\nu} \delta_{\nu',\nu} - \frac{1}{p_0} \int d\mathbf{x} \frac{1}{r_{12}} \phi_{\nu'}^* \phi_\nu. \quad (105)$$

With the help of equations (37), (102) and (105), we can rewrite (104) in the form

$$\begin{vmatrix} \sqrt{2}b_g^{-1} + T'_{1,1} - p_0 & T'_{1,2} \\ T'_{2,1} & \sqrt{2}b_u^{-1} + T'_{2,2} - p_0 \end{vmatrix} = 0, \quad (106)$$

where we have assumed that ϕ_1 and ϕ_2 are normalized according to the requirements of equations (13) and (14), and where

$$T'_{1,1} \equiv -\frac{1}{p_0} \int d\mathbf{x} \frac{1}{r_{12}} |\varphi_g(\mathbf{x}_1)|^2 |\varphi_g(\mathbf{x}_2)|^2,$$

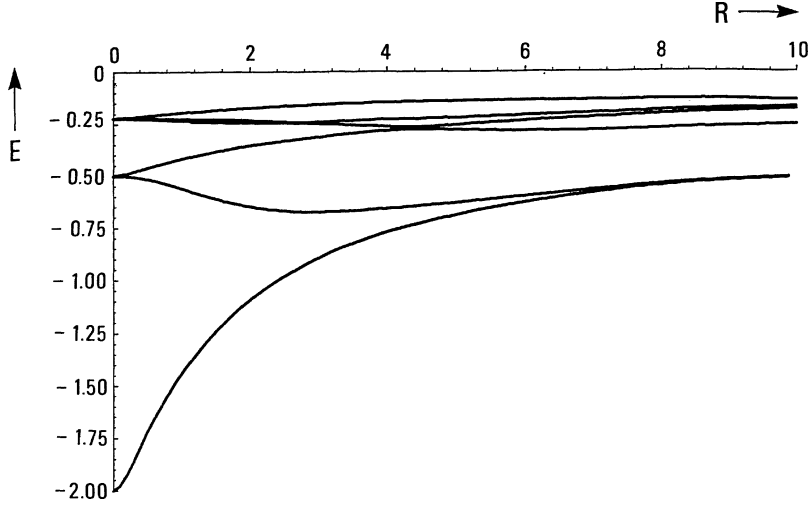


Figure 3. One-electron energies, $\varepsilon_\mu = -1/(2b_\mu^2)$, in Hartrees, as functions of the internuclear separation, R , in atomic units, for an electron moving in the field of two protons. The curves were obtained by solving the one-electron secular equation (99). The lowest curve corresponds to the $\sigma_g 1s$ state, while the next-lowest corresponds to $\sigma_u^* 1s$.

$$T'_{2,2} \equiv -\frac{1}{p_0} \int dx \frac{1}{r_{12}} |\varphi_u(\mathbf{x}_1)|^2 |\varphi_u(\mathbf{x}_2)|^2,$$

$$T'_{1,2} = T'_{2,1} \equiv -\frac{1}{p_0} \int dx \frac{1}{r_{12}} \varphi_g(\mathbf{x}_1) \varphi_u(\mathbf{x}_1) \varphi_g(\mathbf{x}_2) \varphi_u(\mathbf{x}_2). \quad (107)$$

If we wish to obtain a rough picture of the behaviour of the roots of equation (106), we can represent the interelectron repulsion integrals by the approximation

$$T'_{1,1} \approx T'_{2,2} \approx -\frac{1}{2\sqrt{2}} \left[\frac{5}{8} + f(s) \right],$$

$$T'_{1,2} = T'_{2,1} \approx -\frac{1}{2\sqrt{2}} \left[\frac{5}{8} - f(s) \right], \quad (108)$$

where

$$s \equiv k_\mu R = \frac{p_0}{\sqrt{2}} |\mathbf{X}_1 - \mathbf{X}_2| \quad (109)$$

and

$$f(s) \equiv \frac{1}{s} - \left(\frac{24 + 33s + 18s^2 + 4s^3}{24s} \right) e^{-2s}. \quad (110)$$

The reasoning behind the approximation shown in equation (108) is as follows: The $\sigma_g 1s$ one-electron molecular Sturmian can be represented approximately by

$$\varphi_g(\mathbf{x}_j) \approx \mathcal{N} [\chi_{1s}(\mathbf{x}_j - \mathbf{X}_1) + \chi_{1s}(\mathbf{x}_j - \mathbf{X}_2)], \quad (111)$$

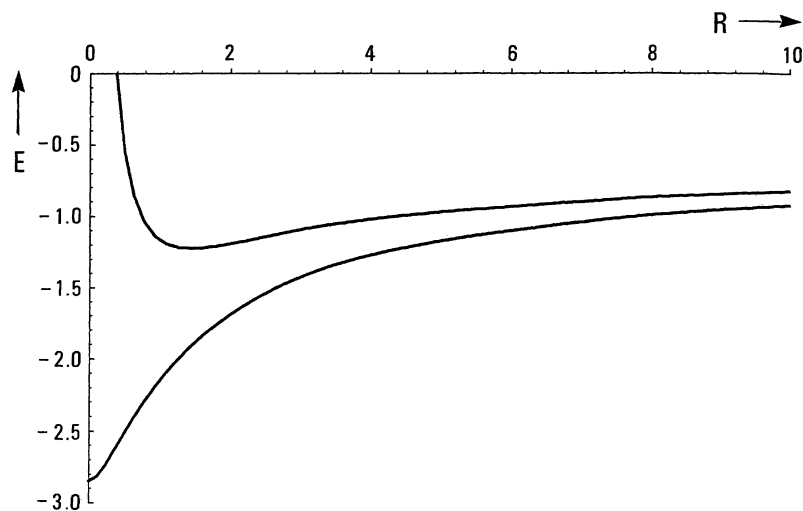


Figure 4. The ground-state electronic energy, $-p_0^2/2$, and the total energy, $-p_0^2/2 + 1/R$, for the H_2 molecule as functions of the internuclear separation, R , calculated by solving the Sturmian secular equation (106).

where \mathcal{N} is a normalization constant chosen in such a way that ϕ_1 fulfills equations (13) and (14). In the united-atom limit, $\mathbf{X}_1 = \mathbf{X}_2 = 0$, $\mathcal{N} = 1/2$, $\varphi_g(\mathbf{x}_j) = \chi_{1s}(\mathbf{x}_j)$ and, making use of our previous result for helium, we obtain

$$T'_{1,1} = -\frac{1}{p_0} \int dx \frac{1}{r_{12}} |\chi_{1s}(\mathbf{x}_1)|^2 |\chi_{1s}(\mathbf{x}_2)|^2 = -\frac{5}{8\sqrt{2}}. \quad (112)$$

In the separated-atom limit, $|\mathbf{X}_1 - \mathbf{X}_2| \rightarrow \infty$, $\mathcal{N} = 1/\sqrt{2}$ and

$$T'_{1,1} = -\frac{1}{4p_0} \int dx \frac{1}{r_{12}} |\chi_{1s}(\mathbf{x}_1 - \mathbf{X}_1) + \chi_{1s}(\mathbf{x}_1 - \mathbf{X}_2)|^2 \\ \times |\chi_{1s}(\mathbf{x}_2 - \mathbf{X}_1) + \chi_{1s}(\mathbf{x}_2 - \mathbf{X}_2)|^2 = -\frac{1}{2\sqrt{2}} \left[\frac{5}{8} + \frac{1}{s} \right]. \quad (113)$$

It can be seen that the approximation for $T'_{1,1}$ in equation (108) yields exact values both in the united-atom limit and in the separated-atom limit; and these two limits are joined by a smooth curve derived by means of the Mullikin approximation. The derivation of the other approximate interelectron repulsion integrals is similar; but it should be noted that $T'_{2,2}$ is exact only in the separated-atom limit. For calculating the ground state of the hydrogen molecule, this defect does not matter, since ϕ_2 does not enter the ground-state wave function appreciably as the united-atom limit is approached. Figure 4 shows the electronic energy and total energy of the hydrogen molecule ground state as functions of the internuclear separation, R , calculated using the approximate interelectron repulsion integrals of equation (108). The calculation gives an equilibrium bond distance of $R = 1.46$ atomic units which can be compared with the experimental value, $R = 1.40$ atomic units. It seems promising that the

rough calculation outlined above gives reasonable results, since the accuracy of the calculation could undoubtedly be improved by using more Sturmian basis functions and by improving the approximation for the interelectron repulsion integrals. The special feature introduced by using many-electron Sturmians in molecular calculations is the automatic optimization of the orbital exponents k_μ through equations (23), (38) and (99). On the hand, the size parameter of the system is not known until the calculation is complete: In the example of H_2 discussed above, we pick a value of s ; we solve the secular equations (99) and (23); and finally, from (38) and $s = k_\mu R$, we obtain the value of R to which the electronic energy $E = -p_0^2/2$ corresponds. This delay in the knowledge of R is not a disadvantage, however, if we wish to generate curves such as the ones shown in figures 3 and 4. In conclusion, it seems likely that the use of many-electron Sturmians will prove to be a useful alternative to the usual methods for treating electron correlation.

Many-particle Sturmians were discussed by Avery and Herschbach in references [6] and [9]; but in these references, the basis sets were constructed from solutions to the d -dimensional hydrogenlike wave equation. The new feature introduced in reference [1] and generalized in the present paper is a method for constructing many-electron Sturmians based on the actual external potential experienced by a set of electrons. The convergence then becomes very much more rapid, only a modest number of basis functions being needed for an accurate representation of a many-electron system. Because of this rapid convergence, because of the elimination of the kinetic energy term, the avoidance of the Hartree–Fock approximation, and the automatic optimization of the orbital exponents, direct solution of the many-electron Schrödinger equation using many-electron Sturmians may one day replace the SCF approach in quantum chemistry.

References

- [1] V. Aquilanti and J. Avery, Chem. Phys. Letters 267 (1997) 1.
- [2] V. Aquilanti, S. Cavalli and C. Coletti, Preprint (1996).
- [3] V. Aquilanti, S. Cavalli, C. Coletti, D. de Fazio and G. Grossi, in: *New Methods in Quantum Theory*, eds. C.A. Tsipis, V.S. Popov, D.R. Herschbach and J.S. Avery (Kluwer, Dordrecht, 1996).
- [4] V. Aquilanti, S. Cavalli, C. Coletti and G. Grossi, Chem. Phys. 209 (1996) 405.
- [5] V. Aquilanti, S. Cavalli and D. de Fazio, J. Phys. Chem. 99 (1995) 15694.
- [6] J. Avery, *Hyperspherical Harmonics; Applications in Quantum Theory* (Kluwer, Dordrecht, 1989).
- [7] J. Avery, in: *Conceptual Trends in Quantum Chemistry*, eds. E.S. Kryachko and J.L. Calais (Kluwer, Dordrecht, 1994), pp. 135–169.
- [8] J. Avery and T.B. Hansen, Int. J. Quantum Chem. 60 (1996) 201.
- [9] J. Avery and D.R. Herschbach, Int. J. Quantum Chem. 41 (1992) 673.
- [10] L. Ballot and M. Fabre de la Ripelle, Ann. Phys. (N.Y.) 127 (1980) 62.
- [11] E. Clementi, J. Chem. Phys. 38 (1963) 996.
- [12] M. Fabre de la Ripelle, Rev. Roum. Phys. 14 (1969) 1215.
- [13] M. Fabre de la Ripelle and J. Navarro, Ann. Phys. (N.Y.) 123 (1979) 185.
- [14] M. Fabre de la Ripelle, Ann. Phys. (N.Y.) 147 (1983) 281.
- [15] V.A. Fock, Z. Phys. 98 (1935) 145.

- [16] V.A. Fock, Bull. Acad. Sci. USSR (1935).
- [17] M. Geller, J. Chem. Phys. 41 (1964) 4006.
- [18] O. Goscinski, Preliminary Research Report No. 217, Quantum Chemistry Group, Uppsala University (1968).
- [19] F.E. Harris and H.H. Michels, Adv. Chem. Phys. 13 (1967) 205.
- [20] B.R. Judd, *Angular Momentum Theory for Diatomic Molecules* (Academic Press, New York, 1975).
- [21] T. Koga and T. Matsuhashi, J. Chem. Phys. 89 (1988) 983.
- [22] H. Monkhorst and B. Jeziorski, J. Chem. Phys. 71 (1979) 5268.
- [23] M. Rotenberg, Adv. At. Mol. Phys. 6 (1970) 233.
- [24] H. Schull and P.O. Löwdin, J. Chem. Phys. 30 (1959) 617.
- [25] T. Shibuya and C.E. Wulfman, Proc. Roy. Soc. A286 (1965) 376.
- [26] E.J. Weniger, J. Math. Phys. 26 (1985) 276.