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Can Coulomb Sturmians Be Used as a Basis for *N*-Electron Molecular Calculations?[†]

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A method is proposed for using isoenergetic configurations formed from many-center Coulomb Sturmians as a basis for calculations on *N*-electron molecules. Such configurations are solutions to an approximate *N*-electron Schrödinger equation with a weighted potential, and they are thus closely analogous to the Goscinskian configurations that we have used previously to study atomic spectra. We show that when the method is applied to diatomic molecules, all of the relevant integrals are pure functions of the parameter $s = kR$, and therefore they can be evaluated once and for all and stored.

Introduction

Since the 1959 paper by Shull and Löwdin,[1] Coulomb Sturmians have found many successful applications in atomic physics.[2−12] Their completeness combined with good convergence properties make them suitable for representing orbitals of electrons in screened Coulomb potentials.

The importance of Coulomb Sturmians in atomic physics suggests that it would be desirable to extend their use to molecular orbital theory. The momentum-space application of many-center Coulomb Sturmians to molecular calculations was pioneered by Shibuya and Wulfman,[13] Aquilanti and co-workers in Perugia, Italy,[14−19] and by Koga's group in Muroan, Japan.[20,21] Aquilanti and his group have been especially known for their deep mathematical investigations of the relationships between the properties of Sturmians and hyperangular momentum theory.

Molecular calculations with Coulomb Sturmians have been confined to one-electron problems. However, in the present paper, we propose a method for using isoenergetic *N*-electron configurations based on Coulomb Sturmians to treat many-center many-electron problems. We show that when this method is applied to diatomic molecules, all of the relevant integrals are pure functions of the parameter $s = kR$, where k is the exponent common to the one-electron basis set and R is the internuclear distance. Closed-form expressions for the integrals can be calculated once and for all, with s and the nuclear charges Z_a and Z_b left as parameters. We believe this to give molecular orbitals based on Coulomb Sturmians a strong advantage compared to other exponential type orbitals.

Coulomb Sturmians on a Single Center

Coulomb Sturmians have the form

$$\chi_\mu(\mathbf{x}_j) = R_{n,l}(t_j)\, Y_{l,m}(\theta_j,\phi_j) \tag{1}$$

where $t_j \equiv kr_j$ and

$$\mu \equiv (n, l, m) \tag{2}$$

and where the functions $\chi_\mu(\mathbf{x}_j)$ satisfy

$$\left[-\frac{1}{2}\nabla_j^2 + \frac{k^2}{2} - \frac{nk}{r_j}\right]\chi_\mu(\mathbf{x}_j) = 0 \tag{3}$$

They obey the potential-weighted orthogonality relation:

$$\int d^3x_j\, \chi^*_{\mu'}(\mathbf{x}_j)\frac{1}{r_j}\chi_\mu(\mathbf{x}_j) = \frac{k}{n}\delta_{\mu'\mu} \tag{4}$$

From eqs 3 and 4, it follows that

$$\int d^3x_j\, \chi^*_{\mu'}(\mathbf{x}_j)\left[-\frac{1}{2}\nabla_j^2 + \frac{k^2}{2}\right]\chi_\mu(\mathbf{x}_j) = k^2\delta_{\mu'\mu} \tag{5}$$

Many-Center Coulomb Sturmians in Molecular Calculations

To use a many-center Coulomb Sturmian basis set to treat molecules, we introduce the notation

$$\chi_\tau(\mathbf{x}) \equiv \chi_\mu(\mathbf{x} - \mathbf{X}_a) \tag{6}$$

for an orbital centered on nucleus a, where

$$\tau \equiv (a, l, m, n) \tag{7}$$

In a molecule, the one-electron nuclear attraction potential has the form

$$v(\mathbf{x}_j) = -\sum_a \frac{Z_a}{|\mathbf{x}_j - \mathbf{X}_a|} \tag{8}$$

We can build up solutions to the one-electron equation

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$$\left[-\frac{1}{2}\nabla_j^2 + \frac{k^2}{2} + \beta_\nu v(\mathbf{x}_j)\right]\varphi_\zeta(\mathbf{x}_j) = 0 \tag{9}$$

from superpositions of many-center Coulomb Sturmians:

$$\varphi_\zeta(\mathbf{x}_j) = \sum_\tau \chi_\tau(\mathbf{x}_j)C_{\tau\zeta} \tag{10}$$

Thus we have

$$\sum_\tau \left[-\frac{1}{2}\nabla_j^2 + \frac{k^2}{2} + \beta_\nu v(\mathbf{x}_j)\right]\chi_\tau(\mathbf{x}_j)C_{\tau\zeta} = 0 \tag{11}$$

Taking the scalar product with a conjugate Coulomb Sturmian yields the 1-electron secular equations:

$$\sum_\tau \int d^3x_j\, \chi^*_{\tau'}(\mathbf{x}_j)\left[-\frac{1}{2}\nabla_j^2 + \frac{k^2}{2} + \beta_\nu v(\mathbf{x}_j)\right]\chi_\tau(\mathbf{x}_j)C_{\tau\zeta} = 0 \tag{12}$$

If we let

$$\mathscr{G}_{\tau'\tau} \equiv \frac{1}{k^2}\int d^3x_j\, \chi^*_{\tau'}(\mathbf{x}_j)\left[-\frac{1}{2}\nabla_j^2 + \frac{k^2}{2}\right]\chi_\tau(\mathbf{x}_j) \tag{13}$$

and

$$\mathscr{W}_{\tau'\tau} \equiv -\frac{1}{k}\int d^3x_j\, \chi^*_{\tau'}(\mathbf{x}_j)\, v(\mathbf{x}_j)\, \chi_\tau(\mathbf{x}_j) \tag{14}$$

then the one-electron secular equations take the form

$$\sum_\tau \left[\mathscr{W}_{\tau'\tau} - \frac{k}{\beta_\nu}\mathscr{G}_{\tau'\tau}\right]C_{\tau\zeta} = 0 \tag{15}$$

The integrals $\mathscr{G}_{\tau'\tau}$ are the well-studied Shibuya–Wulfman integrals, which can be generated using a variety of algorithms. It can be shown that $\mathscr{W}_{\tau'\tau}$ and $\mathscr{G}_{\tau'\tau}$ are related through the sum rule:[20,21]

$$\mathscr{W}_{\tau'\tau''} = \sum_\tau \mathscr{G}_{\tau'\tau}\frac{Z_a}{n}\mathscr{G}_{\tau\tau''} \tag{16}$$

In eq 16, $\tau = (a, \mu)$ runs over all the atoms a in the molecule and the full Coulomb Sturmian basis set centered at $\mathbf{X}_a$. If the basis set is truncated, the relationship is only approximate. We now introduce the matrix

$$\mathbf{K}_{\tau'\tau} \equiv \sqrt{\frac{Z_{a'}Z_a}{n'n}}\,S_{\tau'\tau} \tag{17}$$

which we can call the *Koga matrix* to honor the important contributions of Professor Toshikatsu Koga and his co-workers. Then the sum rule can be rewritten as

$$\mathscr{W}_{\tau'\tau} = \sqrt{\frac{n'n}{Z_{a'}Z_a}}\sum_{\tau''}\mathbf{K}_{\tau'\tau''}\mathbf{K}_{\tau''\tau} \tag{18}$$

Substituting this into the one-electron secular equations we obtain

$$\sum_\tau \left[\sum_{\tau''}\boldsymbol{K}_{\tau'\tau''}\boldsymbol{K}_{\tau''\tau} - \frac{k}{\beta_\nu}\boldsymbol{K}_{\tau'\tau}\right]C_{\tau\zeta} = 0 \tag{19}$$

Now suppose that we have a set of coefficients $C_{\tau\zeta}$ that satisfy

$$\sum_\tau \left[\boldsymbol{K}_{\tau'\tau} - \frac{k}{\beta_\nu}\delta_{\tau'\tau}\right]C_{\tau\zeta} = 0 \tag{20}$$

Then

$$\sum_\tau K_{\tau'\tau}C_{\tau\zeta} = \frac{k}{\beta_\nu}C_{\tau'\zeta} \tag{21}$$

If we substitute this into eq 19 and carry out the sum over τ, we obtain 20. Thus we can see that if the coefficients $C_{\tau\zeta}$ satisfy eq 20, then the one-electron secular eq 15 will also be satisfied, provided that the basis set is complete. Otherwise, solutions to eq 20 are approximate solutions to eq 15. Solution of the secular eq 20 also gives us solutions to eq 9. When the basis set is truncated, the 1-electron secular eqs 15 and 20 give slightly different results. In the case of diatomic molecules, we can evaluate $\mathscr{W}$ directly without using eq 16 or 18, as we will show in eqs 59–62, and so we can choose between eqs 15 and 20. Because of overcompleteness, eq 15 breaks down numerically for small internuclear distances R but gives superior results to eq 20 for large separations. In contrast, eq 20 does not suffer from overcompleteness and becomes progressively more accurate as R approaches zero. Thus the two forms of the 1-electron secular equations complement each other. Calculated energies using eqs 15 and 20 in the appropriate ranges are shown in Tables 1 and 2.

Molecular Calculations Using the Isoenergetic Configurations $\Phi_\nu(\mathbf{x})$

We now introduce the N-electron configurations which are Slater determinants of the form

$$\Phi_\nu(\mathbf{x}) = |\varphi_{\zeta_1}\varphi_{\zeta_2}...\varphi_{\zeta_N}| \tag{22}$$

Since the individual molecular orbitals satisfy 9, the configurations $\Phi_\nu(\mathbf{x})$ are solutions to the separable N-electron equation:

$$\sum_{j=1}^{N}\left[-\frac{1}{2}\nabla_j^2 + \frac{k^2}{2} + \beta_\nu v(\mathbf{x_j})\right]\Phi_\nu(\mathbf{x}) = 0 \tag{23}$$

which can also be written in the form

$$\left[\sum_{j=1}^{N}\left(-\frac{1}{2}\nabla_j^2 + \frac{k^2}{2}\right) + \beta_\nu V_0(\mathbf{x})\right]\Phi_\nu(\mathbf{x}) = 0 \tag{24}$$

where

$$V_0(\mathbf{x}) = \sum_{j=1}^{N} v(\mathbf{x}_j) \tag{25}$$

We would like to use these configurations to build up solutions to the *N*-electron Schrödinger equation

$$\left[\sum_{j=1}^{N}\left(-\frac{1}{2}\nabla_j^2 + \frac{k^2}{2}\right) + V(\mathbf{x})\right]\Psi_\kappa(\mathbf{x}) = 0 \tag{26}$$

with

$$V(\mathbf{x}) = \sum_{j=1}^{N} v(\mathbf{x}_j) + \sum_{i>j}^{N}\sum_{j=1}^{N}\frac{1}{r_{ij}} \tag{27}$$

and with

$$E_\kappa = -\sum_{j=1}^{N}\frac{k^2}{2} = -\frac{Nk^2}{2} \tag{28}$$

Thus we write

$$\Psi_\kappa(\mathbf{x}) = \sum_{\nu}\Phi_\nu(\mathbf{x})B_{\nu\kappa} \tag{29}$$

Substituting this into the *N*-electron Schrödinger equation, and taking the scalar product with a conjugate configuration, we obtain the secular equations:

$$\sum_{\nu}\int \mathrm{d}x\, \Phi^*_{\nu'}(\mathbf{x})\left[\sum_{j=1}^{N}\left(-\frac{1}{2}\nabla_j^2 + \frac{k^2}{2}\right) + V(\mathbf{x})\right]\Phi_\nu(\mathbf{x})B_{\nu\kappa} = 0 \tag{30}$$

We now introduce a *k*-independent matrix representing the total potential based on the configurations $\Phi_\nu(\mathbf{x})$:

$$T^{(N)}_{\nu'\nu} \equiv -\frac{1}{k}\int \mathrm{d}x\, \Phi^*_{\nu'}(\mathbf{x})\, V(\mathbf{x})\, \Phi_\nu(\mathbf{x}) \tag{31}$$

and another *k*-independent matrix

$$\mathscr{G}^{(N)}_{\nu'\nu} \equiv \frac{1}{k^2}\int \mathrm{d}x\, \Phi^*_{\nu'}(\mathbf{x})\sum_{j=1}^{N}\left(-\frac{1}{2}\nabla_j^2 + \frac{k^2}{2}\right)\Phi_\nu(\mathbf{x}) \tag{32}$$

In terms of these matrices, the secular equations become

$$\sum_{\nu}[\mathbf{T}^{(N)}_{\nu'\nu} - k\mathscr{G}^{(N)}_{\nu'\nu}]\mathbf{B}_{\nu\kappa} = 0 \tag{33}$$

Solving eq 33, we obtain k for each state κ and thus the energy $E_\kappa = -Nk^2/2$. For a given state κ, the value of k then determines the weighting factors β_{ν_1}, β_{ν_2}, ... needed to make each configuration Φ_{ν_1}, Φ_{ν_2}, ... correspond to the same energy E_κ.

Solving the Secular Equations

The matrix $T^{(N)}_{\nu'\nu}$ can be constructed from the 1-electron components using the generalized Slater−Condon rules.[12] From eq 10 we have

$$\tilde{m}_{\zeta'\zeta} \equiv \int \mathrm{d}^3x_j\, \varphi^*_{\zeta'}(\mathbf{x}_j)\, \varphi_\zeta(\mathbf{x}_j) = \sum_{\tau'}\sum_{\tau} C^*_{\tau'\zeta'}m_{\tau'\tau}C_{\tau\zeta} \tag{34}$$

where

$$m_{\tau'\tau} \equiv \int \mathrm{d}^3x_j\, \chi^*_{\tau'}(\mathbf{x}_j)\, \chi_\tau(\mathbf{x}_j) \tag{35}$$

are displaced Sturmian overlap integrals. Similarly

$$\tilde{v}_{\zeta'\zeta} \equiv \int \mathrm{d}^3x_j\varphi^*_{\zeta'}(\mathbf{x}_j)v(\mathbf{x}_j)\varphi_\zeta(\mathbf{x}_j) = -k\sum_{\tau'}\sum_{\tau} C^*_{\tau'\zeta'}\mathscr{M}_{\tau'\tau}C_{\tau\zeta} \tag{36}$$

and also

$$\tilde{\mathscr{G}}_{\zeta'\zeta} \equiv \sum_{\tau'}\sum_{\tau} C^*_{\tau'\zeta'}\mathscr{G}_{\tau'\tau}C_{\tau\zeta} = \frac{\beta_\nu}{k^2}\tilde{v}_{\zeta'\zeta} \tag{37}$$

To build the *N*-electron matrices $T^{(N)}_{\nu'\nu}$ and $\mathscr{G}^{(N)}_{\nu'\nu}$ and solve eq 33, we must first obtain the coefficients $C_{\tau\zeta}$ by solving eq 15 or 20. In the case of diatomic molecules, we begin by picking a value of the parameter $s = kR$, where R is the interatomic distance and k is the exponent of the Coulomb Sturmian basis set. Neither R nor k is known at this point, but only their product s. As we shall see below, for the diatomic case, all of the integrals involved in eqs 15 and 20 are pure functions of s. Having chosen s, we can thus solve the one-electron secular equations and obtain the coefficients $C_{\tau\zeta}$ and the spectrum of ratios k/β_ν. We are then able to solve eq 33, which gives us a spectrum of k-values, and thus energies $-Nk^2/2$, and the eigenvectors $\mathbf{B}_{\nu\kappa}$. From a k-value, we also get the unscaled distance $R = s/k$. We repeat the procedure for a range of s-values and interpolate to find the solutions as functions of R.

In the case of polyatomic molecules, one can choose a set of angles between the nuclei; these are left fixed under scaling of the coordinate system. The procedure is then similar to that described for the diatomic case.

Evaluation of Shibuya−Wulfman and Sturmian Overlap Integrals

The two-center Sturmian overlap integrals can conveniently be evaluated in momentum space, using the relationships[12]

$$m_{\tau'\tau} \equiv \int \mathrm{d}^3x_j\, \chi^*_{\tau'}(\mathbf{x}_j)\, \chi_\zeta(\mathbf{x}_j) = \int \mathrm{d}^3p\, \chi^{t*}_{\tau'}(\mathbf{p})\, \chi^t_\tau(\mathbf{p}) \tag{38}$$

and

$$\chi^t_\tau(\mathbf{p}) = M(p)\, Y_{n-1,l,m}(\mathbf{u})\mathrm{e}^{-\mathrm{i}\mathbf{p}\cdot\mathbf{X}_a} \tag{39}$$

Here

$$M(p) \equiv \frac{4k^{5/2}}{(k^2 + p^2)^2} \tag{40}$$

while $Y_\mu(\mathbf{u})$ is a 4-dimensional hyperspherical harmonic. In eq 39, $\mathbf{u}$ is a unit vector that defines Fock's projection of momentum space onto the surface of a 4-dimensional hypersphere.[22]

$$\mathbf{u} = (u_1, u_2, u_3, u_4) = \left(\frac{2kp_1}{k^2 + p^2}, \frac{2kp_2}{k^2 + p^2}, \frac{2kp_3}{k^2 + p^2}, \frac{k^2 - p^2}{k^2 + p^2}\right) \tag{41}$$

Substituting eq 39 into eq 38, we obtain

$$m_{\tau'\tau} = \int \mathrm{d}^3p \, \frac{16k^5}{(k^2 + p^2)^4} Y^*_{n'-1,l',m'}(\mathbf{u}) \, Y_{n-1,l,m}(\mathbf{u}) \mathrm{e}^{\mathbf{ip\cdot R}} \tag{42}$$

where $\mathbf{R} \equiv \mathbf{X}_{a'} - \mathbf{X}_a$. The integral can be evaluated directly using the expansion of a plane wave in terms of spherical Bessel functions and Legendre polynomials:

$$\mathrm{e}^{\mathbf{ip\cdot R}} = \sum_{l=0}^{\infty} i^l (2l + 1) \, j_l(pR) \, P_l(\hat{\mathbf{p}}\cdot\hat{\mathbf{R}}) \tag{43}$$

For example, $Y_{0,0,0} = 1/(2\pi^2)^{1/2}$, and therefore

$$m_{(a',1,0,0),(a,1,0,0)} = \frac{2}{\pi}\int_0^\infty dp \frac{16k^5p^2}{(k^2 + p^2)^4} j_0(pR) = e^{-s}\left(1 + s + \frac{s^2}{3}\right) \tag{44}$$

where $s \equiv kR$. Alternatively, we can convert the integral in eq 42 into a hyperangular integral using the relationship[12]

$$\mathrm{d}^3p = \mathrm{d}\Omega \left(\frac{k^2 + p^2}{2k}\right)^3 \tag{45}$$

Then eq 42 becomes

$$m_{\tau'\tau} = \int \mathrm{d}\Omega \, \frac{2k^2}{(k^2 + p^2)} Y^*_{n'-1,l',m'}(\mathbf{u}) \, Y_{n-1,l,m} \mathrm{e}^{\mathbf{ip\cdot R}} \tag{46}$$

or

$$m_{\tau'\tau} = \int \mathrm{d}\Omega \, (1 + u_4) Y^*_{n'-1,l',m'}(\mathbf{u}) \, Y_{n-1,l,m} \mathrm{e}^{\mathbf{ip\cdot R}} \tag{47}$$

Similarly, the Shibuya–Wulfman integrals can be expressed in the form[13]

$$\mathscr{G}_{\tau'\tau} = \int \mathrm{d}\Omega \, Y^*_{n'-1,l',m'}(\mathbf{u}) \, Y_{n-1,l,m} \mathrm{e}^{\mathbf{ip\cdot R}} \tag{48}$$

We then make use of the relationship[9]

$$\int \mathrm{d}\Omega \, Y_{n-1,l,m} \mathrm{e}^{\mathbf{ip\cdot R}} = (2\pi)^{3/2} f_{n,l}(s) \, Y_{l,m}(\hat{\mathbf{s}}) \tag{49}$$

where $Y_{l,m}$ is an ordinary 3-dimensional spherical harmonic and where

$$\mathbf{s} = \{s_x, s_y, s_z\} \equiv k\mathbf{R} \tag{50}$$

The function $f_{n,l}(s)$ is defined by

$$k^{3/2} f_{n,l}(s) \equiv R_{n,l}(s) - \frac{1}{2}\sqrt{\frac{(n - l)(n + l + 1)}{n(n + 1)}} R_{n+1,l}(s) - \frac{1}{2}\sqrt{\frac{(n + l)(n - l - 1)}{n(n - 1)}} R_{n-1,l}(s) \tag{51}$$

where $R_{n,l}$ is the radial function of the Coulomb Sturmians given in eq 1, and where

$$R_{n-1,l}(s) \equiv 0 \quad \text{if} \quad l > n - 1 \tag{52}$$

Similarly, the integral

$$m_{(a',1,0,0),(a,n,l,m)} = \frac{1}{\sqrt{2}\pi}\int \mathrm{d}^3p \, \frac{16k^5}{(k^2 + p^2)^4} Y_{n-1,l,m}(\mathbf{u}) \mathrm{e}^{\mathbf{ip\cdot R}} \tag{53}$$

can be written in the form

$$m_{(a',1,0,0),(a,n,l,m)} = \sqrt{4\pi} g_{n,l}(s) \, Y_{l,m}(\hat{\mathbf{s}}) \tag{54}$$

For other values of τ', $m_{\tau'\tau}$ can be found by resolving $Y^*_{n'-1,l',m'}(\mathbf{u}) \, Y_{n-1,l,m}(\mathbf{u})$ into a sum of 4-dimensional hyperspherical harmonics. The function $g_{n,l}(s)$ is given by

$$g_{n,l}(s) \equiv f_{n,l}(s) - \frac{1}{2}\sqrt{\frac{(n - l)(n + l + 1)}{n(n + 1)}} f_{n+1,l}(s) - \frac{1}{2}\sqrt{\frac{(n + l)(n - l - 1)}{n(n - 1)}} f_{n-1,l}(s) \tag{55}$$

where we define

$$f_{n-1,l}(s) \equiv 0 \quad \text{if} \quad l > n - 1 \tag{56}$$

The coupling coefficients that appear here are the ones needed for resolving $(1 + u_4)Y_{n-1,l,m}$ into a sum of 4-dimensional hyperspherical harmonics. The problem of evaluating both the Shibuya–Wulfman integrals and the two-center Coulomb Sturmian overlap integrals thus reduces to the problem of resolving the product $Y^*_{n'-1,l',m'} Y_{n-1,l,m}$ into a sum of 4-dimensional hyperspherical harmonics. This can be done either using 4-dimensional Wigner coefficients, a method pioneered by Prof. Vincenzo Aquilanti and his co-workers,[14,15,18,19,23] or alternatively, using the harmonic projection methods studied by us.[3,6,7,12] For example, since $Y_{0,0,0}(\mathbf{u}) = 1/(2\pi^2)^{1/2}$ we have

$$\mathscr{G}_{(a',1,0,0),(a,n,l,m)} = \frac{1}{\sqrt{2\pi^2}} \int d\Omega\, Y_{n-1,l,m}(\mathbf{u}) e^{i\mathbf{p}\cdot\mathbf{R}} = \sqrt{4\pi} f_{n,l}(s)\, Y_{l,m}(\hat{\mathbf{s}}) \quad (57)$$

Evaluation of the Nuclear Attraction Integrals, $\tau'\tau$

From the definition of the nuclear attraction integrals (14) and from (8), we have

$$\mathscr{W}_{\tau'\tau} \equiv -\frac{1}{k} \int d^3x_j\, \chi^*_{\tau'}(\mathbf{x}_j)\, v(\mathbf{x}_j)\, \chi_\tau(\mathbf{x}_j) = \frac{1}{k} \int d^3x_j\, \chi^*_{\tau'}(\mathbf{x}_j) \sum_a \frac{Z_a}{|\mathbf{x}_j - \mathbf{X}_a|} \chi_\tau(\mathbf{x}_j) \quad (58)$$

For diatomic molecules, this becomes

$$\mathscr{W}_{\tau'\tau} = \frac{1}{k} \int d^3x_j\, \chi^*_{\tau'}(\mathbf{x}_j) \left[\frac{Z_1}{|\mathbf{x}_j - \mathbf{X}_1|} + \frac{Z_2}{|\mathbf{x}_j - \mathbf{X}_2|} \right] \chi_\tau(\mathbf{x}_j) \quad (59)$$

For the case of diatomic molecules, we are thus faced with three types of integrals:

$$I^{(1)}_{\mu'\mu} = \frac{1}{k} \int d^3x_j\, \chi^*_{\mu'}(\mathbf{x}_j) \frac{1}{|\mathbf{x}_j - \mathbf{X}|} \chi_\mu(\mathbf{x}_j) \quad (60)$$

$$\begin{aligned} I^{(2)}_{\mu'\mu} &= \frac{1}{k} \int d^3x_j\, \chi^*_{\mu'}(\mathbf{x}_j) \frac{1}{|\mathbf{x}_j - \mathbf{X}|} \chi_\mu(\mathbf{x}_j - \mathbf{X}) \\ &= \frac{1}{k} \int d^3x_j\, \chi^*_{\mu'}(\mathbf{x}_j) \left[-\frac{1}{2}\nabla_j^2 + \frac{k^2}{2} \right] \chi_\mu(\mathbf{x}_j - \mathbf{X}) \end{aligned} \quad (61)$$

and

$$I^{(3)}_{\mu'\mu} = \frac{1}{k} \int d^3\, x_j \chi^*_{\mu'}(\mathbf{x}_j) \frac{1}{|\mathbf{x}_j|} \chi_\mu(\mathbf{x}_j) = \frac{\delta_{\mu'\mu}}{n} \quad (62)$$

Integrals of the type $I^{(1)}_{\mu'\mu}$ can be evaluated by expanding $1/|\mathbf{x}_j - \mathbf{X}|$ in terms of Legendre polynomials, or alternatively by introducing the Fourier integral representation of $1/|\mathbf{x}_j - \mathbf{X}|$, while integrals of the type $I^{(2)}_{\mu'\mu}$ can be expressed in terms of Shibuya−Wulfman integrals. Integrals of the type $I^{(3)}_{\mu'\mu}$ are easily evaluated using eq 5.

Two-Center Interelectron Repulsion Integrals for Coulomb Sturmians

If $\rho_1(\mathbf{x} - \mathbf{X}_a)$ and $\rho_2(\mathbf{x}' - \mathbf{X}_{a'})$ are two electron density distributions, centered respectively on nuclei at the positions $\mathbf{X}_a$ and $\mathbf{X}_{a'}$, the interelectron repulsion between them is given by the integral

$$J = \int d^3x \int d^3x'\, \rho_1(\mathbf{x} - \mathbf{X}_a) \frac{1}{|\mathbf{x} - \mathbf{x}'|} \rho_2(\mathbf{x}' - \mathbf{X}_{a'}) \quad (63)$$

If we introduce the Fourier transform representation

$$\frac{1}{|\mathbf{x} - \mathbf{x}'|} = \frac{1}{2\pi^2} \int d^3p\, \frac{1}{p^2} e^{i\mathbf{p}\cdot(\mathbf{x}-\mathbf{x}')} \quad (64)$$

we can rewrite J in the form

$$J = 4\pi \int d^3p\, \frac{1}{p^2} \rho_1^t(\mathbf{p})\, \rho_2^t(-\mathbf{p}) e^{i\mathbf{p}\cdot\mathbf{R}} \quad (65)$$

where $\mathbf{R} = \mathbf{X}_{a'} - \mathbf{X}_a$ and

$$\rho_j^t(\mathbf{p}) = \frac{1}{(2\pi)^{3/2}} \int d^3x\, \rho_j(\mathbf{x}) e^{-i\mathbf{p}\cdot\mathbf{x}} \qquad j = 1, 2 \quad (66)$$

The Fourier transforms of products of Coulomb Sturmians are easy to obtain. For example,

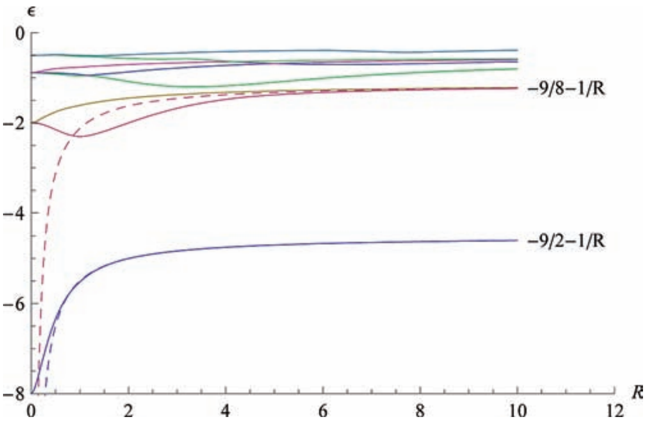

Figure 1. Electronic energies of LiH^{3+} obtained as functions of R from eqs 15 and 20 with $\beta_\nu = 1$ and $\varepsilon = -k^2/2$. The z-axis was taken in the direction of the internuclear separation, and only basis functions with $m = 0$ were used. The dotted lines show the asymptotic behaviors $-9/2 - 1/R$ and $-9/8 - 1/R$ of the lowest three energies (see Table 2). As the LiH^{3+} ion dissociates, the single electron of the system follows the Li nucleus. The electronic energy of the ion approaches that of Li^{2+}, −9/2 hartree, plus the energy of the electron in the attractive potential of the distant H$^+$ ion, $-1/R$.

TABLE 1: Energies as Functions of Internuclear Distances for the Lowest Orbitals of H$_2^+$, Calculated Using a Basis with 10 Coulomb Sturmians on Each Nucleus (Atomic Units Used Throughout)

	energy		
R	σ_g 1s	σ_g 2s	σ_u^* 2s
0	−2.00000	−0.500000	−0.500000
0.1	−1.97822	−0.500613	−0.496003
0.2	−1.92846	−0.502489	−0.48914
0.4	−1.80006	−0.509921	−0.470570
0.6	−1.67030	−0.522165	−0.452714
0.8	−1.55305	−0.538910	−0.437248
1	−1.45032	−0.559748	−0.423120
2	−1.10220	−0.667529	−0.360727
3	−0.910878	−0.701418	−0.318789
4	−0.796074	−0.695551	−0.289563
5	−0.724413	−0.677292	−0.265364
6	−0.678631	−0.657311	−0.247421
8	−0.627569	−0.623606	−0.221687
10	−0.600578	−0.599901	−0.204651
$R \to \infty$	$-1/2 - 1/R$	$-1/2 - 1/R$	$-1/8 - 1/R$

If $\rho_{(1s)^2}(\mathbf{x}) = [\chi_{1,0,0}(\mathbf{x})]^2$ then

$$\rho^t_{(1s)^2}(\mathbf{p}) = \frac{4\sqrt{2}k^4}{(4k^2 + p^2)^2\pi^{3/2}} \tag{67}$$

The integrals in eq 65 can be evaluated analytically. For example,

$$\begin{aligned} J_{\langle(1s)^2|(1s)^2\rangle} &= (4\pi)^2 \int_0^\infty \mathrm{d}p \left[\frac{4\sqrt{2}k^4}{(4k^2 + p^2)^2\pi^{3/2}}\right]^2 j_0(pR) \\ &= \frac{24 + \mathrm{e}^{-2kR}(-24 - kR(33 + 2kR(9 + 2kR)))}{24R} \end{aligned} \tag{68}$$

This is the Coulomb integral representing the interelectron repulsion between a $(1s)^2$ Coulomb Sturmian charge density located at the point $\mathbf{X}_a$ and a $(1s)^2$ density located at $\mathbf{X}_{a'}$. When $R \to 0$, the integral approaches $5k/8$, while for large R, it approaches $1/R$. Notice that if we divide it by k, the integral is a pure function of $s = kR$, and this is true of all integrals of this type representing interactions between products of Coulomb Sturmians. Similarly, we find that

$$\frac{1}{k}J_{\langle(1s)^2|(2s)^2\rangle} = \frac{1}{s} + \frac{\mathrm{e}^{-2s}}{240s}[-240 - s(390 + s(300 + s(145 + 2s(25 + 6s))))] \tag{69}$$

and so on. To systematize integrals of this type, we note that

$$\begin{aligned} \mathscr{J}_{n,l}\left(\frac{p}{2k}\right) &\equiv \int_0^\infty \mathrm{d}t\, t^n \mathrm{e}^{-2t} j_l(pt/k) \\ &= \left(\frac{p}{2k}\right)^l \frac{(n + l)!\,{}_2F_1[(a|b|c - (p/2k)^2}{(2l + 1)!!2^{n+1}[1 + (p/2k)^2]^n} \end{aligned} \tag{70}$$

where

$$\begin{aligned} a &\equiv (l - n + 1)2 \\ b &\equiv (l - n + 1)2 \\ c &\equiv l + 3/2 \end{aligned}$$

and that the Fourier transform of the partial density $\rho_{jlm}(\mathbf{x}) = 4k^3(kr)^j\mathrm{e}^{-2kr}Y_{l,m}(\hat{\mathbf{x}})$ is therefore given by

$$\rho^t_{jlm}(\mathbf{p}) = \frac{1}{(2\pi)^{3/2}}\int \mathrm{d}^3x\, \mathrm{e}^{-\mathrm{i}\mathbf{p}\cdot\mathbf{r}}[4k^3(kr)^j\mathrm{e}^{-2kr}Y_{l,m}(\hat{\mathbf{x}})] = 4\sqrt{\frac{2}{\pi}}(-\mathrm{i})^l Y_{l,m}(\hat{\mathbf{p}})\mathscr{J}_{j+2,l}\left(\frac{p}{2k}\right) \tag{71}$$

TABLE 2: Energies as Functions of Internuclear Distances for the Lowest Orbitals of the LiH^{3+} Ion (Figure 1)

	energy		
R	σ_g 1s	σ_g 2s	σ_u^* 2s
0	−8.00000	−2.00000	−2.00000
0.1	−7.77863	−2.00743	−1.96276
0.2	−7.38734	−2.02913	−1.91086
0.4	−6.64066	−2.10542	−1.80342
0.6	−6.10336	−2.19682	−1.71865
0.8	−5.75353	−2.27294	−1.66012
1	−5.52094	−2.30570	−1.61374
2	−5.00204	−2.00153	−1.45288
3	−4.83370	−1.67811	−1.37216
4	−4.75011	−1.48006	−1.32336
5	−4.70005	−1.37882	−1.29064
6	−4.66669	−1.32515	−1.26717
8	−4.62501	−1.26748	−1.23576
10	−4.60000	−1.23586	−1.21571
$R \to \infty$	$-9/2 - 1/R$	$-9/8 - 1/R$	$-9/8 - 1/R$

From eq 65 we can see that the Coulomb interaction between two charge densities of this type, located respectively on the centers $\mathbf{X}_a$ and $\mathbf{X}_{a'}$ will be given by

$$\mathbf{J}_{j'l'm',jlm} = 4\pi \int \mathrm{d}^3p\, \frac{1}{p^2}\rho^t_{j'l'm'}(\mathbf{p})\, \rho^t_{jlm}(-\mathbf{p})\mathrm{e}^{\mathrm{i}\mathbf{p}\cdot\mathbf{R}} \tag{72}$$

Substituting eq 10 into eq 11, we have

$$J_{j'l'm',jlm} = 4\pi\left(4\sqrt{\frac{2}{\pi}}\right)^2(-\mathrm{i})^{l'+l}\int_0^\infty \mathrm{d}p\, \mathscr{J}_{j'+2,l'}\left(\frac{p}{2k}\right)\mathscr{J}_{j+2,l}\left(\frac{p}{2k}\right) \times \int \mathrm{d}\Omega_p\, Y_{l',m'}(\mathbf{p})\, Y_{l,m}(-\hat{\mathbf{p}})\mathrm{e}^{\mathrm{i}\mathbf{p}\cdot\mathbf{R}} \tag{73}$$

To perform the momentum-space angular integration, we expand the plane wave in terms of Legendre polynomials and spherical Bessel functions:

$$\mathrm{e}^{\mathrm{i}\mathbf{p}\cdot\mathbf{R}} = \sum_{l''=0}^{\infty} i^{l''}(2l'' + 1)j_{l''}(pR)\, P_{l''}(\hat{\mathbf{p}}\cdot\hat{\mathbf{R}}) \tag{74}$$

We then obtain

$$\int \mathrm{d}\Omega_p\, Y_{l',m'}(\hat{\mathbf{p}})\, Y_{l,m}(-\hat{\mathbf{p}})\mathrm{e}^{\mathrm{i}\mathbf{p}\cdot\mathbf{R}} = \sum_{l''=0}^{\infty} i^{l''}(2l'' + 1)j_{l''}(pR)\int \mathrm{d}\Omega_p\, Y_{l',m'}(\hat{\mathbf{p}})\, Y_{l,m}(-\hat{\mathbf{p}})\, P_{l''}(\hat{\mathbf{p}}\cdot\hat{\mathbf{R}}) \tag{75}$$

which can be rewritten in the form[12]

$$\int \mathrm{d}\Omega_p\, Y_{l',m'}(\hat{\mathbf{p}})\, Y_{l,m}(-\hat{\mathbf{p}})\mathrm{e}^{\mathrm{i}\mathbf{p}\cdot\mathbf{R}} = 4\pi\sum_{l''=0}^{\infty} i^{l''}j_{l''}(pR)\, O_{l''}[Y_{l',m'}(\hat{\mathbf{R}})\, Y_{l,m}(-\hat{\mathbf{R}})] \tag{76}$$

where $O_{l''}$ is an operator that projects out the part of an angular function corresponding to angular momentum l''. This gives us finally the result:

$$J_{j'l'm',jlm} = (4\pi)^2\left(4\sqrt{\frac{2}{\pi}}\right)^2(-\mathrm{i})^{l'+l}\sum_{l''=0}^{\infty} i^{l''}O_{l''}[Y_{l',m'}(\hat{\mathbf{R}})\, Y_{l,m}(-\hat{\mathbf{R}})] \times \int_0^\infty \mathrm{d}p\, \mathscr{J}_{j'+2,l'}\left(\frac{p}{2k}\right)\mathscr{J}_{j+2,l}\left(\frac{p}{2k}\right)j_{l''}(pR) \tag{77}$$

The integrals $J_{j'l'm',jlm}$ can be precalculated analytically and stored. When $\hat{\mathbf{R}}$ is in the direction of the z-axis, only the case where $m' = -m$ gives a nonzero result. From the stored pieces, we can assemble the integrals in which we are really interested. We let

$$\rho_1(\mathbf{x}) \equiv \chi^*_{\mu_1}(\hat{\mathbf{x}})\,\chi_{\mu_2}(\hat{\mathbf{x}}) = \sum_{j=l_1+l_2}^{n_1+n_2-2}\ \sum_{l=|l_1-l_2|}^{l_1+l_2} \rho_{j,l,m_2-m_1}(\mathbf{x})C^{j,l}_{\mu_1,\mu_2} \tag{78}$$

while

$$\rho_2(\mathbf{x}') \equiv \chi^*_{\mu_3}(\hat{\mathbf{x}}')\,\chi_{\mu_4}(\hat{\mathbf{x}}') = \sum_{j'=l_3+l_4}^{n_3+n_4-2}\ \sum_{l'=|l_3-l_4|}^{l_3+l_4} \rho_{j',l',m_4-m_3}(\mathbf{x}')\boldsymbol{C}^{j',l'}_{\mu_3,\mu_4} \tag{79}$$

and where we have used the abreviation $\mu_i \equiv (n_i, l_i, m_i)$. Then the following formula assembles the integral in which we are interested from the stored pieces:

$$J_{\mu_1,\mu_2,\mu_3,\mu_4} = \sum_{j=l_1+l_2}^{n_1+n_2-2}\ \sum_{l=|l_1-l_2|}^{l_1+l_2}\ \sum_{j'=l_3+l_4}^{n_3+n_4-2}\ \sum_{l'=|l_3-l_4|}^{l_3+l_4} J_{j,l,m_2-m_1,j',l',m_4-m_3} C^{j,l}_{\mu_1,\mu_2} C^{j',l'}_{\mu_3,\mu_4} \tag{80}$$

We now need to calculate the coefficients $C^{j,l}_{\mu_1,\mu_2}$ and $C^{j',l'}_{\mu_3,\mu_4}$. If we introduce the notation:

$$R_{n_1,l_1}(kr)\,R_{n_2,l_2}(kr) = \sum_{j=l_1+l_2}^{n_1+n_2-2} 4k^3(kr)^j \mathrm{e}^{-2kr} \alpha^j_{n_1,l_1,n_2,l_2} \tag{81}$$

and

$$Y^*_{l_1,m_1}(\mathbf{x})\,Y_{l_2,m_2}(\hat{\mathbf{x}}) = \sum_{l=|l_1-l_2|}^{l_1+l_2} Y_{l,m_2-m_1}(\hat{\mathbf{x}})\beta^l_{l_1,m_1,l_2,m_2} \tag{82}$$

then

$$C^{j,l}_{\mu_1,\mu_2} = \alpha^j_{n_1,l_1,n_2,l_2}\beta^l_{l_1,m_1,l_2,m_2} \tag{83}$$

Integrals involving densities formed from two-center products of Coulomb Sturmians are more difficult to evaluate, but they too are pure functions of s when divided by k. To treat these integrals, one can, for example, use the Mulliken approximation. Within the framework of the Mulliken approximation, it is possible, in the case of diatomic molecules, to find coefficients $\tilde{C}^{j,l,1}_{\zeta,\zeta'}(s)$ and $\tilde{C}^{j,l,2}_{\zeta,\zeta'}(s)$ such that

$$\rho_{\zeta,\zeta'}(\mathbf{x}) \equiv \varphi^*_{\zeta}(\mathbf{x})\,\varphi_{\zeta'}(\mathbf{x}) \approx \sum_j \sum_l [\rho_{j,l,m'-m}(\mathbf{x} - \mathbf{X}_1)\tilde{\mathrm{C}}^{j,l,1}_{\zeta,\zeta'}(s) + \rho_{j,l,m'-m}(\mathbf{x} - \mathbf{X}_2)\tilde{\mathrm{C}}^{j,l,2}_{\zeta,\zeta'}(s)] \tag{84}$$

In other words, it is possible to express the density due to a product of two molecular orbitals directly in terms of the partial densities in a manner analogous to eq 78. This was done in the small example given below.

N-Electron Diatomic Molecules

Let us now specialize to the case of diatomic molecules. Without loss of generality, we can choose the z-axis along the direction of internuclear separation. Then, expressing $\mathbf{s}$ in spherical polar coordinates, we have $\theta = 0$, and the spherical harmonics $Y_{lm}(\hat{\mathbf{s}})$ vanish unless $m = 0$; thus also the ϕ-dependence disappears. From eqs 50 and 51 it follows that the Shibuya−Wulfman integrals $\mathscr{G}_{\tau'\tau}$ are sums of terms, each of whose angular dependence is a spherical harmonic $Y_{lm}(\mathbf{s})$, but as we have just seen, these spherical harmonics will simply be constants. Therefore, the Shibuya−Wulfman integrals, for the diatomic case, are pure functions of $s = kR$. By similar arguments, it is easy to see that also $m_{\tau'\tau}$, $\mathscr{W}_{\tau'\tau}$ and the interelectron repulsion integrals become pure functions of s.

Precomputed Integrals. It is possible to precalculate closed form expressions for $\mathscr{G}_{\tau'\tau}$, $\mathscr{W}_{\tau'\tau}$ and $m_{\tau'\tau}$, where $\mathscr{G}$ and m depend only on s, and where $\mathscr{W}$ depends on s and the nuclear charges Z_a and Z_b.

We have calculated closed form expressions for the matrix elements $\mathscr{G}_{\tau'\tau}$, $\mathscr{W}_{\tau'\tau}$, and $m_{\tau'\tau}$ for the case of diatomic molecules for all valid (n, l, m), (n', l', m') with $n, n' \leq 5$, for all valid $(n, l, 0)$, $(n', l', 0)$ with $n, n' \leq 7$ and for all valid $(n, 0, 0)$, $(n', 0, 0)$ when $n, n' \leq 20$. From the expressions, we have generated very fast C-code, which is made available through a shared library. The implementation, which will be described in a separate publication, can be downloaded from http://sturmian.kvante.org/diatomic.

It contains both the precomputed integrals and the programs that precalculate them using harmonic projection methods and that generate fast C-code. The work of precalculating the interelectron repulsion integrals is in progress.

Calculations on Diatomic Systems. Using the precomputed integrals discussed above, we can with very little additional effort study any N-electron diatomic molecule, obtaining properties as functions of R. We can ensure that the functions will be defined in the desired range of R-values by choosing a sufficiently large range for s, as is done in step 2 below. The following solves a diatomic problem in the range $[0; R_{\max}]$:

1. Choose nuclear charges Z_a, Z_b and one-electron bases $\{\mu_1, ..., \mu_{M_a}\}$ on center a and $\{\mu_1, ..., \mu_{M_b}\}$ on center b. Choose also the N-electron basis set of configurations $\{\nu_1, ..., \nu_M\}$.
2. Let $k_{\max} = (-2E_0/N)^{1/2}$, where E_0 is some lower bound to the energy; for example, the energy of the noninteracting system. This makes sure that $k_{\max}R_{\max} \geq kR_{\max}$.
3. Choose a number of sample points $S = \{0, s_1, ..., s_m, k_{\max}\cdot R_{\max}\} \subset [0; R_{\max}]$.
4. Now, for each sample point $s \in S$, do the following:
    (a) Build the one-electron matrices $\mathscr{G}(\mathrm{Z}_a, \mathrm{Z}_b, s)$ and $\mathscr{W}(\mathrm{Z}_a, \mathrm{Z}_b, s)$ and solve eq 15 or 20. This gives us the roots k/β_ν and coefficients $C_{\tau\zeta}$ for s.
    (b) Use $C_{\tau\zeta}$ to construct $T^{(N)}_{\nu'\nu}$ and $\mathscr{G}^{(N)}_{\nu'\nu}$, by way of eqs 36, 37, and 84, and solve eq 33, yielding $B_{\nu\kappa}(s)$ and the energies $E_\kappa(s) = -Nk^2(s)/2$. For each state κ of the system, we also obtain a corresponding distance $R_\kappa = s/k(s)$.
5. For the states of interest, construct tables listing R-values and the corresponding properties. Finally, interpolating the tables will give smooth functions of the properties in terms of R, ensured to be defined in the range $[0; R_{\max}]$.

A Simple Example: The HeH $^+$ Ion. To illustrate the method, we performed a rough calculation on the HeH^+ ion, making use of the Mulliken approximation to treat two-center densities. For simplicity, we used only one configuration. Our Coulomb Sturmian basis set was also minimal, and used only

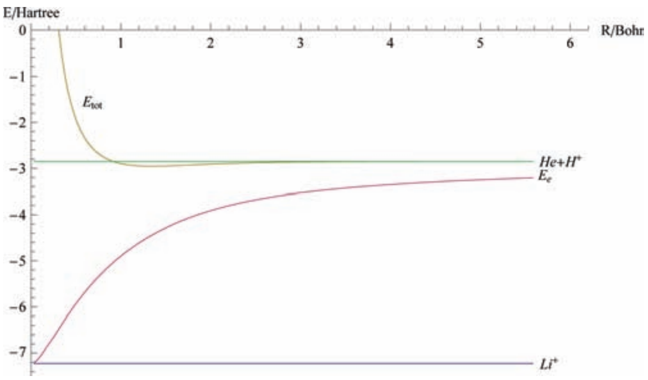

Figure 2. Electronic energy E_e and the total energy E_{tot} of the HeH $^+$ ion as a function of the internuclear separation $R = s/k$. The calculation was performed with a single configuration using a one-electron basis set consisting of 6 Coulomb Sturmians. For $R \to 0$, the electronic energy approaches the energy calculated for the Li $^+$ ion using the Generalized Sturmian Method with a single configuration.[1] In the separated atom region, the total energy approaches that of He when calculated in the same way. Our calculation shows a shallow minimum at $R = 1.35$ Bohrs, which can be compared to the equilibrium bond length of 1.46 Bohrs obtained in a benchmark calculation by Wolniewicz.[24]

six (n, l, m)-values: (1, 0, 0), (2, 0, 0), (2, 1, 0), (3, 0, 0), (3, 1, 0) and (3, 2, 0). We used the single configuration $\Phi_1 = |\varphi_1\varphi_{\bar{1}}|$ where φ_1 and $\varphi_{\bar{1}}$ are the lowest spin-up and spin-down orbitals found by solving eq 15. Figure 2 shows the resulting ground-state energy as a function of the internuclear separation, with and without the internuclear repulsion term; i.e., it shows the electronic energy and the total energy. In the united-atom limit, the electronic energy reduces to $-1849/256 = -0.722266$ hartree. This is the Li$^+$ energy that is obtained by substituting $Z = 3$ into the formula for the ground-state energies of the 2-electron isoelectronic atomic series, calculated with a single Goscinskian configuration:[1]

$$E = -\frac{1}{2}\left(Z\sqrt{2} - \frac{5}{8\sqrt{2}}\right)^2 \qquad (85)$$

In the separated-atom limit, the total energy approaches the value $-729/256 = -2.84766$ hartree, which is the value obtaifned from eq 85 with $Z = 2$, i.e., the approximate ground-state energy of helium calculated with a single Goscinskian configuration. We can see from this that as HeH$^+$ dissociates, both electrons follow the helium nucleus. This is why the dissociation of HeH$^+$ can be described with approximate correctness by a single configuration, which is famously not possible for **H**$_2$. Our rough calculation shows a shallow minimum of the total energy at an internuclear separation of 1.34781 Bohrs. This calculated equilibrium bond length is to be compared with the benchmark value,[24] 1.46324 Bohrs. We believe that a more refined calculation, using the present method with a richer basis of Coulomb Sturmians and a larger number of configurations, would lead to closer agreement. With more configurations, we would also obtain the excited states of the system. Greater accuracy could be obtained by avoiding the Mulliken approximation.

Discussion

Two-center Coulomb Sturmians have long been used in 1-electron calculations on diatomic molecules, but let us try to answer the question of our title: Can Coulomb Sturmians be used as basis functions for N-electron molecular calculations? We believe that the method proposed in this paper can make this possible, and that many-center Coulomb Sturmians have some advantages over other ETO basis functions. If we apply the method to diatomic molecules, all of the relevant integrals are pure functions of the parameter $s = kR$ and nuclear charges Z_a and Z_b. The matrices $\mathscr{W}_{\tau'\tau}$, $\mathscr{G}_{\tau'\tau}$, $K_{\tau'\tau}$, and $m_{\tau'\tau}$ can be evaluated once and for all and stored with general nuclear charges and general s. Furthermore, the Fock projection and the theory of hyperspherical harmonics can be used for the efficient evaluation of these integrals. The two-center interelectron repulsion integrals are also pure functions of the parameter $s = kR$, and they too can be evaluated once and for all and stored; however, this work remains to be completed. The isoenergetic N-electron configurations proposed here are closely analogous to the Goscinskian configurations,[2] which we have successfully used to calculate the spectra of atoms and atomic ions.[3−12] Thus the proposed method seems promising to us, and we hope to explore it further.

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