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Dimensional scaling and the quantum mechanical many-body problem

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Summary. A growing repertoire of electronic structure methods employ the spatial dimension D as an interpolation or scaling parameter. It is advantageous to transform the Schrödinger equation to remove all dependence on D from the Jacobian volume element and the Laplacian operator; this introduces a centrifugal term, quadratic in D, that augments the effective potential. Here we explicitly formulate this procedure for S states of an arbitrary many-particle system, in two variants. One version reduces the Laplacian to a quasicartesian form, and is particularly suited to evaluating the exactly solvable $D \to \infty$ limit and perturbation expansions about this limit. The other version casts the Jacobian and Laplacian into the familiar forms for $D = 3$, and is particularly suited to calculations employing conventional Rayleigh–Ritz variational methods.

Key words: Dimensional scaling – Quantum theory – Schrödinger equation – Many-body problem

1. Introduction

During the past few years, application of dimensional scaling to the quantum theory of atomic and molecular structure has yielded new computational methods and conceptual insights [1–5]. This new approach requires solving the many-particle Schrödinger equation in a D-dimensional coordinate space. Since all vectors are endowed with D cartesian components, the Laplacian operator and the Jacobian volume element are modified, but the potential energy retains the same form as for $D = 3$. Exact solutions can be found in the $D \to \infty$ limit, regardless of the number of electrons. This limit can be related to the physical dimension, $D = 3$, by using a perturbation expansion in terms of $1/D$, or by other means. Exact solutions can also be obtained at $D \to 1$ for two-electron systems. This permits interpolation between the dimensional limits; e.g., to a very

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good approximation the correlation energy is just a linear function of $1/D$ for the ground states of two-electron atoms [2].

When taking D as variable, it is expedient to transform the many-particle Schrödinger equation to remove the D dependence from the Jacobian J and the Laplacian operator. This amounts to setting $\psi = J^{-1/2}\phi$ and solving, not for the wavefunction ψ, but rather for ϕ, the square root of the distribution function. Such a transformation gives rise to a centrifugal potential, U, which contains the explicit D dependence, simply a quadratic factor. On introducing hydrogenic dimension-scaled units, U and the Coulombic potential V become independent of D, whereas the remaining kinetic energy terms scale as $1/D^2$. Thus, as D becomes large, the kinetic energy terms are suppressed, and the distribution function of the system is sharply localized at the minimum of the total effective potential, $U+V$. At this point, referred to as the *Lewis structure*, the particles all assume fixed positions in the scaled coordinates. Expansion of the potential about the Lewis structure yields a normal mode problem for harmonic vibrations of the particles, which are referred to as the *Langmuir vibrations*. For smaller values of D, the expansion gives a systematic method for constructing solutions to arbitrary order in $1/D$. The procedure provides a convenient and intuitively appealing way to treat both electronic correlation and corrections to the Born–Oppenheimer approximation.

In this paper, we refine and extend the method previously used by Loeser [4] to simplify the Schrödinger equation for N particles in D dimensions and to evaluate the centrifugal potential. Our chief result is a new variant that permits dimensional scaling to be readily incorporated in conventional Rayleigh–Ritz variational calculations. In order to illustrate and motivate the main features in the simplest way, however, we first consider a two-electron atom with fixed nucleus in D space. After presenting the general case, we discuss some aspects of the Lewis structure and Langmuir vibrational modes, first for three particles and then for N particles.

2. Two-electron atom in *D* dimensions

The wavefunction for S states involves only three internal coordinates (for a fixed nucleus), usually taken as R_1 and R_2, the electron-nucleus radii, and θ, the included angle. In Hartree–Bohr atomic units, the Schrödinger equation is:

$$(-\tfrac{1}{2}\Delta + V)\psi = E\psi, \tag{2.1}$$

with V the Coulombic potential. The Laplacian operator takes the form $\Delta = \Delta_{R_1} + \Delta_{R_2} + \Delta_\theta$, with:

$$\begin{aligned}\Delta_{R_i} &= \frac{1}{R_i^{D-1}}\frac{\partial}{\partial R_i}\left(R_i^{D-1}\frac{\partial}{\partial R_i}\right)\\ &= \frac{\partial^2}{\partial R_i^2} + \frac{(D-1)}{R_i}\frac{\partial}{\partial R_i}, \qquad i = 1, 2\end{aligned} \tag{2.2}$$

and

$$\Delta_\theta = \left(\frac{1}{R_1^2} + \frac{1}{R_2^2}\right)\tilde{\Delta}_\theta, \tag{2.3a}$$

where

$$\tilde{\Delta}_\theta = \frac{1}{\sin^{D-2}\theta}\frac{\partial}{\partial\theta}\left(\sin^{D-2}\theta\frac{\partial}{\partial\theta}\right)$$

$$= \frac{\partial^2}{\partial\theta^2} + (D-2)\cot\theta\frac{\partial}{\partial\theta}. \tag{2.3b}$$

Likewise, the radial and angular parts are separable in the Jacobian factor:

$$J = J_R J_\theta = (R_1 R_2)^{D-1}\sin^{D-2}\theta. \tag{2.4}$$

It would be awkward to compare solutions for different D, since both ψ and J depend on dimension. Hence we seek a transformation, $\psi = \chi\phi$, with the function χ chosen to simplify $\Delta\phi$ and to render the Jacobian for ϕ independent of D. Two physically motivated choices are apparent. (i) We can make the Jacobian for the ϕ function become just unity by taking $\chi = J^{-1/2}$, since then the distribution function $|\phi|^2 = J|\psi|^2$ incorporates the full Jacobian. This choice has been used in most previous work [1] with D scaling. (ii) We can instead factor the Jacobian as $J = J_3 J_{D-3}$ where:

$$J_3 = (R_1 R_2)^2 \sin\theta, \tag{2.5a}$$

$$J_{D-3} = (R_1 R_2 \sin\theta)^{D-3}, \tag{2.5b}$$

so J_3 has the form familiar for $D = 3$. We may retain the J_3 portion as the Jacobian for the ϕ function by taking $\chi = J_{D-3}^{-1/2}$, thereby tucking the D-dependent portion into $|\phi|^2 = J_{D-3}|\psi|^2$, with the distribution function now given by $J_3|\phi|^2 = J|\psi|^2$.

The radial and angular components of the transformed Laplacian have the form:

$$\chi^{-1}\Delta_R\chi\phi = A_R\frac{\partial^2\phi}{\partial R^2} + \frac{B_R}{R}\frac{\partial\phi}{\partial R} + \frac{C_R}{R^2}\phi \tag{2.6}$$

and

$$\chi^{-1}\tilde{\Delta}_\theta\chi\phi = A_\theta\frac{\partial^2\phi}{\partial\theta^2} + B_\theta\frac{\partial\phi}{\partial\theta} + C_\theta\phi. \tag{2.7}$$

The resulting Schrödinger equation for the ϕ function is:

$$(T + U + V)\phi = E\phi, \tag{2.8}$$

where $T = T_{R_1} + T_{R_2} + T_\theta$ denotes the kinetic energy terms involving differential operators and U denotes the centrifugal potential, given by:

$$T_R = -\frac{1}{2}\left(A_R\frac{\partial^2}{\partial R^2} + \frac{B_R}{R}\frac{\partial}{\partial R}\right), \tag{2.9}$$

$$T_\theta = -\frac{1}{2}\left(\frac{1}{R_1^2} + \frac{1}{R_2^2}\right)\left(A_\theta\frac{\partial^2}{\partial\theta^2} + B_\theta\frac{\partial}{\partial\theta}\right), \tag{2.10}$$

and

$$U = -\frac{1}{2}\left(\frac{1}{R_1^2} + \frac{1}{R_2^2}\right)(C_R + C_\theta). \tag{2.11}$$

Table 1 gives the coefficients that appear in Eqs. (2.6)–(2.11), for both Cases (i) and (ii). The Jacobian for the ϕ function, denoted $\tilde{J}$, is also shown; this is determined by $\tilde{J} = J|\chi|^2$. Table 2 gives the corresponding centrifugal potentials. For Case (i), we note that T contains only second derivatives, and thus has simplified to a quasicartesian form, commensurate with the unit Jacobian for the ϕ function. For Case (ii) the T operator also contains first derivatives but is identical in form to the Laplacian for $D = 3$, commensurate with J_3 as the Jacobian for the ϕ function. Furthermore, the difference between the Case (i) centrifugal potentials for general D is equal to the centrifugal potential for Case (ii):

$$U_D(\mathrm{i}) - U_3(\mathrm{i}) = U_D(\mathrm{ii}). \tag{2.12}$$

In practice, Case (i) is particularly suited to evaluating the exactly solvable $D \to \infty$ limit and dimensional perturbation expansions about this limit [3, 5]. However, Case (ii) has a major advantage for calculations employing conventional variational methods. Since the Schrödinger equation for Case (ii) is precisely the same as for $D = 3$, except for the addition of the scalar U term, *any*

Table 1. Laplacian components and Jacobian factors for two-electron atom

Radius, R:	A_R	B_R	C_R	$\tilde{J}_R$
χ_R	1	$(D-1) + \frac{2R}{\chi}\frac{\partial\chi}{\partial R}$	$(D-1)\frac{R}{\chi}\frac{\partial\chi}{\partial R} + \frac{R^2}{\chi}\frac{\partial^2\chi}{\partial R^2}$	
$R^{-\alpha}$	1	$(D-1-2\alpha)$	$-\alpha(D-2-\alpha)$	$R^{D-1-2\alpha}$
(i) $\alpha = \frac{1}{2}(D-1)$	1	0	$-\left(\frac{D-1}{2}\right)\left(\frac{D-3}{2}\right)$	1
(ii) $\alpha = \frac{1}{2}(D-3)$	1	2	$-\left(\frac{D-3}{2}\right)\left(\frac{D-1}{2}\right)$	R^2
Angle, θ:	A_θ	B_θ	C_θ	$\tilde{J}_\theta$
χ_θ	1	$(D-2)\cot\theta + \frac{2}{\chi}\frac{\partial\chi}{\partial\theta}$	$(D-2)\frac{\cot\theta}{\chi}\frac{\partial\chi}{\partial\theta} + \frac{1}{\chi}\frac{\partial^2\chi}{\partial\theta^2}$	
$(\sin\theta)^{-\beta}$	1	$(D-2-2\beta)\cot\theta$	$\beta[(D-2-\beta) - (D-3-\beta)\csc^2\theta]$	$(\sin\theta)^{D-2-2\beta}$
(i) $\beta = \frac{1}{2}(D-2)$	1	0	$\left(\frac{D-2}{2}\right)\left[\left(\frac{D-2}{2}\right) - \left(\frac{D-4}{2}\right)\csc^2\theta\right]$	1
(ii) $\beta = \frac{1}{2}(D-3)$	1	$\cot\theta$	$\left(\frac{D-3}{2}\right)\left[\left(\frac{D-1}{2}\right) - \left(\frac{D-3}{2}\right)\csc^2\theta\right]$	$\sin\theta$
cosine, γ:	A_γ	B_γ	C_γ	$\tilde{J}_\gamma$
χ_γ	Γ	$-(D-1)\gamma + 2\frac{\Gamma}{\chi}\frac{\partial\chi}{\partial\gamma}$	$-(D-1)\frac{\gamma}{\chi}\frac{\partial\chi}{\partial\gamma} + \frac{\Gamma}{\chi}\frac{\partial^2\chi}{\partial\gamma^2}$	
$\Gamma^{-\frac{1}{2}\beta}$	Γ	$-(D-1-2\beta)\gamma$	$\beta[(D-2-\beta) - (D-3-\beta)\csc^2\theta]$	$\Gamma^{\frac{1}{2}(D-3)-\beta}$
(iii) $\beta = \frac{1}{2}(D-1)$	Γ	0	$\left(\frac{D-1}{2}\right)\left[\left(\frac{D-3}{2}\right) - \left(\frac{D-5}{2}\right)\csc^2\theta\right]$	Γ^{-1}
(ii) $\beta = \frac{1}{2}(D-3)$	Γ	-2γ	$\left(\frac{D-3}{2}\right)\left[\left(\frac{D-1}{2}\right) - \left(\frac{D-3}{2}\right)\csc^2\theta\right]$	1

Table 2. Centrifugal potential for two-electron atom

Case	$F_D(\theta)$ in $U=\frac{1}{2}\left(\frac{1}{R_1^2}+\frac{1}{R_2^2}\right)F_D(\alpha,\beta;\theta)$
(i) $\alpha=\frac{1}{2}(D-1)$, $\beta=\frac{1}{2}(D-2)$	$-\frac{1}{4}+\left(\frac{D-2}{2}\right)\left(\frac{D-4}{2}\right)\csc^2\theta$
(ii) $\alpha=\beta=\frac{1}{2}(D-3)$	$\left(\frac{D-3}{2}\right)^2\csc^2\theta$
(iii) $\alpha=\beta=\frac{1}{2}(D-1)$	$\left(\frac{D-1}{2}\right)\left(\frac{D-5}{2}\right)\csc^2\theta$

existing computer code can be generalized to D dimensions simply by adding the matrix elements for the centrifugal potential.

The choice of internal coordinates also has a major role. To illustrate this, we transform from the angle θ to its cosine, $\gamma=\cos\theta$. (For many-electron atoms, Loeser [4] found cosines are a felicitous choice.) The angular Laplacian of Eq. (2.3) is then replaced by:

$$\tilde{\Delta}_\gamma=\Gamma\frac{\partial^2}{\partial\gamma^2}-(D-1)\gamma\frac{\partial}{\partial\gamma} \tag{2.13}$$

and the angular factor in the Jacobian of Eq. (2.4) is replaced by:

$$J_\gamma=\Gamma^{(D-3)/2}, \tag{2.14}$$

where $\Gamma=1-\gamma^2=\sin^2\theta$. Again there are two natural choices for the γ-dependent portion of the transformation function, both of the form $\chi_\gamma=\Gamma^{-\beta/2}$. The choice made by Loeser [4], here denoted Case (iii), takes $\beta=\frac{1}{2}(D-1)$, in order to eliminate the first derivative term in T_γ, the transformed kinetic energy analogous to Eq. (2.10). Instead, we advocate Case (ii), with $\beta=\frac{1}{2}(D-3)$, in order to exploit the simple correspondence with $D=3$ results. Tables 1 and 2 include the requisite formulas. Note that, for a given choice for the χ function, transforming from θ to γ does not alter the centrifugal potential but does change the Laplacian and the Jacobian. The Case (ii) policy is to choose χ so that Δ and J for the ϕ function have the $D=3$ form for any choice of coordinates. This ensures that the D-dimensional Hamiltonian for ϕ has the key property,

$$H_D(\text{ii})=H_3(\text{ii})+U_D(\text{ii}). \tag{2.15}$$

This remarkably simple result will hold also for many-particle systems.

3. Schrödinger equation for N particles in D dimensions

We now consider S states for the general case of N particles ($i=1,2,\ldots,N$) with arbitrary masses m_i and charges Z_i. The coordinates can be divided into a set of internal coordinates, $X_1, X_2, \ldots, X_\tau$ (not necessarily orthogonal), and a set of external coordinates, $X_{\tau+1}, X_{\tau+2}, \ldots, X_d$ (which include the Euler angles), where $d=DN$. As $D\to\infty$, the external coordinates become infinitely numerous, while τ, the number of internal coordinates, remains fixed. As none of the particles is necessarily fixed, there are N position vectors, each with D cartesian components: $x_i = (x_{i1}, x_{i2}, \ldots, x_{iD})$. The Schrödinger equation is:

$$\left(-\sum_{i=1}^{N} \frac{1}{2m_i} \Delta_i + V\right)\psi = E\psi, \tag{3.1}$$

where

$$\Delta_i \equiv \sum_{t=1}^{D} \frac{\partial^2}{\partial x_{it}^2}$$

is the Laplacian operator for the ith particle. Since the wavefunction, ψ, for S states depends only on the internal coordinates, we express Δ_i in terms of the internal coordinates:

$$\Delta_i = \sum_{\mu=1}^{\tau}\left(A_i^{\mu}\frac{\partial}{\partial x_\mu} + \sum_{\nu=1}^{\tau} G_i^{\mu\nu}\frac{\partial^2}{\partial X_\mu \partial X_\nu}\right), \tag{3.2}$$

where

$$A_i^{\mu} \equiv \sum_{t=1}^{D} \frac{\partial^2 X_\mu}{\partial x_{it}^2} \tag{3.3}$$

and

$$G_i^{\mu\nu} \equiv \sum_{t=1}^{D} \frac{\partial X_\mu}{\partial x_{it}} \frac{\partial X_\nu}{\partial x_{it}}. \tag{3.4}$$

The corresponding Jacobian J for the transformation to internal coordinates is given by:

$$J = G^{1/2}, \tag{3.5}$$

where G is the determinant of a matrix with elements defined by:

$$G_{\mu\nu}^{i} \equiv \sum_{t=1}^{D} \frac{\partial x_{it}}{\partial X_\mu} \frac{\partial x_{it}}{\partial X_\nu}. \tag{3.6}$$

This matrix is the inverse of that formed by Eq. (3.4). The Laplacian can be rewritten [6] as:

$$\Delta_i = \sum_{\mu,\nu=1}^{\tau}\left\{\left[J^{-1}\frac{\partial}{\partial X_\nu}(JG_i^{\mu\nu})\right]\frac{\partial}{\partial X_\mu} + G_i^{\mu\nu}\frac{\partial^2}{\partial X_\mu \partial X_\nu}\right\}. \tag{3.7}$$

This relates the A_i^{μ} coefficient to $G_i^{\mu\nu}$ and J and their derivatives.

The transformation $\psi = \chi\phi$ brings the Schrödinger equation to the form Eq. (2.8), with the kinetic energy operator given by:

$$T = -\sum_{i=1}^{N}\frac{1}{2m_i}\left[\sum_{\mu,\nu=1}^{\tau} G_i^{\mu\nu}\frac{\partial^2}{\partial X_\mu \partial X_\nu} + \sum_{\mu=1}^{\tau}\left(A_i^{\mu} + 2\sum_{\nu=1}^{\tau} G_i^{\mu\nu}\chi^{-1}\frac{\partial\chi}{\partial X_\nu}\right)\frac{\partial}{\partial X_\mu}\right] \tag{3.8}$$

and the centrifugal energy by:

$$U = -\sum_{i=1}^{N}\frac{1}{2m_i}\sum_{\mu=1}^{\tau}\left(A_i^{\mu}\chi^{-1}\frac{\partial\chi}{\partial X_\mu} + \sum_{\nu=1}^{\tau} G_i^{\mu\nu}\chi^{-1}\frac{\partial^2\chi}{\partial X_\mu \partial X_\nu}\right). \tag{3.9}$$

Following Loeser [4], we take as internal coordinates the radii R_i and cosines γ_{ij} defined by:

$$R_i^2 \equiv \sum_{t=1}^{D} x_{it}^2 \tag{3.10a}$$

and

$$\gamma_{ij} \equiv \boldsymbol{x}_i \cdot \boldsymbol{x}_j / R_i R_j. \tag{3.10b}$$

Then

$$\Delta_i = \Delta_{R_i} + \frac{1}{R_i^2} \tilde{\Delta}_{\gamma_i}, \tag{3.11}$$

where Δ_{R_i} has the same form as Eq. (2.2), and:

$$\tilde{\Delta}_{\gamma_i} = \sum_{j \neq i}^{N} \sum_{k \neq i}^{N} (\gamma_{jk} - \gamma_{ij}\gamma_{ik}) \frac{\partial^2}{\partial \gamma_{ij} \partial \gamma_{ik}} - (D-1) \sum_{j \neq i}^{N} \gamma_{ij} \frac{\partial}{\partial \gamma_{ij}}. \tag{3.12}$$

The Jacobian is given by:

$$J = J_R J_\gamma = (R_1 R_2 \cdots R_N)^{D-1} \Gamma^{(D-N-1)/2}, \tag{3.13}$$

where Γ is the Gramian determinant [7]:

$$\Gamma \equiv |\gamma_{ij}|. \tag{3.14}$$

This form for J can be obtained directly from Eq. (3.6) but can be more simply verified by comparing the first derivative terms in Eqs. (3.2), (3.7), and (3.11). In Appendix A we give some pertinent properties of the Gramian determinant and its derivatives.

Radial and cosine factors in the transformation function are again separable, and we consider functions of the form:

$$\chi = \chi_R \chi_\gamma = (R_1 R_2 \cdots R_N)^{-\alpha} \Gamma^{-\beta/2}, \tag{3.15}$$

analogous to those of Table 1. For the radial part we readily find:

$$\chi^{-1} \Delta_{R_i} \chi \phi = \frac{\partial^2 \phi}{\partial R_i^2} + \frac{(D-1-2\alpha)}{R_i} \frac{\partial \phi}{\partial R_i} - \frac{\alpha(D-2-\alpha)}{R_i^2} \phi. \tag{3.16}$$

This is the same result obtained in Table 1. The cosine part is more involved; we find:

$$\begin{aligned} \chi^{-1} \Delta_{\gamma_i} \chi \phi = {} & \sum_{j \neq i}^{N} \sum_{k \neq i}^{N} (\gamma_{jk} - \gamma_{ij}\gamma_{ik}) \frac{\partial^2 \phi}{\partial \gamma_{ij} \partial \gamma_{ik}} - (D-1) \sum_{j \neq i}^{N} \gamma_{ij} \frac{\partial \phi}{\partial \gamma_{ij}} - \beta \sum_{k \neq i}^{N} S_{ik} \frac{\partial \phi}{\partial \gamma_{ik}} \\ & + \tfrac{1}{2}\beta[(D-1)S_i' + (\tfrac{1}{2}\beta + 1)S_i'' - S_i''']\phi, \end{aligned} \tag{3.17}$$

with

$$S_{ik} = \Gamma^{-1} \sum_{j \neq i}^{N} (\gamma_{jk} - \gamma_{ij}\gamma_{ik}) \frac{\partial \Gamma}{\partial \gamma_{ij}},$$

$$S_i' = \Gamma^{-1} \sum_{j \neq i}^{N} \gamma_{ij} \frac{\partial \Gamma}{\partial \gamma_{ij}},$$

$$S_i'' = \Gamma^{-2} \sum_{j \neq i}^{N} \sum_{k \neq i}^{N} (\gamma_{jk} - \gamma_{ij}\gamma_{ik}) \frac{\partial \Gamma}{\partial \gamma_{ij}} \frac{\partial \Gamma}{\partial \gamma_{ik}},$$

$$S_i''' = \Gamma^{-1} \sum_{j \neq i}^{N} \sum_{k \neq i}^{N} (\gamma_{jk} - \gamma_{ij}\gamma_{ik}) \frac{\partial^2 \Gamma}{\partial \gamma_{ij} \partial \gamma_{ik}}.$$

The sums involving derivatives of Γ are evaluated in Appendix A. Finally, we obtain general expressions for the kinetic energy, $T = T_R + T_\gamma$, with:

$$T_R = -\sum_{i=1}^{N} \frac{1}{2m_i}\left[\frac{\partial^2}{\partial R_i^2} + \frac{(D-1-2\alpha)}{R_i}\frac{\partial}{\partial R_i}\right] \tag{3.18}$$

and

$$T_\gamma = -\sum_{i=1}^{N} \frac{1}{2m_i R_i^2}\left[\sum_{j\neq i}^{N}\sum_{k\neq i}^{N}(\gamma_{ik} - \gamma_{ij}\gamma_{ik})\frac{\partial^2}{\partial\gamma_{ij}\,\partial\gamma_{ik}} - (D-1-2\beta)\sum_{j\neq i}^{N}\gamma_{ij}\frac{\partial}{\partial\gamma_{ij}}\right] \tag{3.19}$$

and the centrifugal energy:

$$U = \sum_{i=1}^{N}\frac{1}{2m_i R_i^2}\left[(\alpha-\beta)(D-2-\alpha-\beta) + \beta(D-N-1-\beta)\frac{\Gamma^{(i)}}{\Gamma}\right], \tag{3.20}$$

where $\Gamma^{(i)}$ is the principal minor formed by deleting from Γ the row and column corresponding to the ith particle. The Jacobian for the ϕ function is given by:

$$\tilde{J} = J|\chi|^2 = (R_1 R_2 \cdots R_N)^{D-1-2\alpha}\Gamma^{(D-N-1-2\beta)}. \tag{3.21}$$

By specifying the values of the exponents α and β of the transformation function of Eq. (3.15) we can now evaluate various cases corresponding to those of Tables 1 and 2. Results for U and $\tilde{J}$ are given in Table 3 for the three cases of chief interest: (i) with $\tilde{J}$ reduced to unity; (ii) with T and $\tilde{J}$ cast in the same form as for $D = 3$; and (iii) with the transformation chosen to eliminate the first derivative terms from the kinetic energy. For (ii) and (iii) the exponents α and β have the same values as for the two-particle system; those for (i) differ because we used γ rather than θ for the N-particle system. For both (ii) and (iii), or whenever $\alpha = \beta$, the centrifugal energy has a quite tidy form:

$$U = \frac{f}{2\Gamma}\sum_{i=1}^{N}\frac{\Gamma^{(i)}}{m_i R_i^2}, \tag{3.22}$$

in which only the D-dependent scale factor f differs. This generalizes the result first obtained by Loeser [4]; his derivation required (iii) and particles with equal mass. For Case (ii) the key result of Eq. (2.15) indeed holds for the N-particle Hamiltonian.

Table 3. Centrifugal potential and Jacobian factors for N-particles

Case	$F_D(\Gamma)$ in $U = \frac{1}{2}\sum_i F_D(\alpha, \beta; \Gamma)/m_i R_i^2$	$\tilde{J}$
(i) $\alpha = \frac{1}{2}(D-1)$, $\beta = \frac{1}{2}(D-N-1)$	$\frac{N}{2}\left(\frac{N}{2}-1\right) + \left(\frac{D-N-1}{2}\right)^2(\Gamma^{(i)}/\Gamma)$	1
(ii) $\alpha = \beta = \frac{1}{2}(D-3)$	$\left(\frac{D-3}{2}\right)\left(\frac{D-2N+1}{2}\right)(\Gamma^{(i)}/\Gamma)$	$\Gamma^{\frac{1}{2}(2-N)}\prod_i R_i^2$
(iii) $\alpha = \beta = \frac{1}{2}(D-1)$	$\left(\frac{D-1}{2}\right)\left(\frac{D-2N-1}{2}\right)(\Gamma^{(i)}/\Gamma)$	$\Gamma^{-\frac{1}{2}N}$

4. The large D regime

To examine the transformed Schrödinger equation in the large-D limit we introduce scaled radii and energy:

$$r_i \equiv R_i/f \quad \text{and} \quad \epsilon \equiv fE, \tag{4.1}$$

where f is the factor, quadratic in D, that appears in the centrifugal potential of Eq. (3.22). Although the precise definition of f depends on the choice of the transformation function, in the limit $D \to \infty$ this becomes inconsequential because $f \to D^2/4$ in any case. We consider a Coulombic potential V, which scales as R^{-1}, whereas both the kinetic energy T and centrifugal potential U scale as R^{-2}. Accordingly, with the scaling adopted in Eq. (4.1), the scaled potentials $V\{r_i, \gamma_{ij}\}$ and $U\{r_i, \gamma_{ij}\}$ become independent of D whereas the scaled $T\{r_i, \gamma_{ij}\}$ contains a factor of f^{-1}. Hence the kinetic energy terms become progressively less and less important as D becomes large; in effect, the mass factors in the scaled T are inflated by a factor f. In the limit $D \to \infty$ only an effective potential $W = U + V$ survives. For our N-particle Coulombic system with arbitrary masses and charges:

$$W \equiv \sum_{i=1}^{N} \left[\frac{\Gamma^{(i)}}{2m_i r_i^2 \Gamma} + \sum_{j=i+1}^{N} \frac{Z_i Z_j}{(r_i^2 + r_j^2 - 2r_i r_j \gamma_{ij})^{1/2}} \right]. \tag{4.2}$$

For $D \to \infty$ the scaled ground-state energy of a bound system becomes:

$$\epsilon_\infty = W\{\bar{r}_i, \bar{\gamma}_{ij}\}, \tag{4.3}$$

where $\{\bar{r}_i, \bar{\gamma}_{ij}\}$ denotes the values of the scaled radii and cosines at which the global minimum of W occurs. The geometrical configuration of the system at this minimum is called [1] the *Lewis structure.* For finite but large values of D we can expand W in a Taylor series about the global minimum, in the manner customary for molecular vibrations [8]. The leading term after the constant, ϵ_∞, is quadratic in the displacements from the minimum and thus defines a normal mode problem. The small vibrations of the system about the global minimum for large D are called [1] the *Langmuir vibrations.*

In the large-D limit any of the variants considered for the transformation function of Eq. (3.15) is simply related to the Jacobian of (3.13) by $\chi \to J^{-1/2}$. Thus, in this limit, ϕ represents the square root of the distribution function, $|\phi|^2 \to J|\psi|^2$, which becomes sharply localized in the neighborhood of the Lewis structure [9]. As D decreases, the Langmuir vibrations about the Lewis structure become anharmonic and rapidly grow in amplitude. Nevertheless, the harmonic oscillator wavefunctions pertaining to the large-D regime can be used to generate recursively the coefficients of a perturbation expansion [5] of ϕ and ϵ in powers of $1/D$.

Electronic structure calculations for atoms usually take the nucleus as fixed at the origin. This has also been done in previous applications of dimensional scaling, except in a treatment of the large-D limit for helium and helium dimuonic atoms by van der Merwe [10, 11]. In our general formulation none of the particles need be considered as fixed and the origin can be chosen arbitrarily; the results should, of course, be independent of the position of the origin.

4.1. Three-particle Lewis structures

As a simple example we consider a three-particle system in which each particle may have a distinct mass and charge. Suppose we adopt cartesian axes such that:

$$\begin{aligned} \boldsymbol{r}_1 &= (a, 0, c_1, c_2, c_3, \dots), \\ \boldsymbol{r}_2 &= (-a', 0, c_1, c_2, c_3, \dots), \\ \boldsymbol{r}_3 &= (0, b, c_1, c_2, c_3, \dots), \end{aligned} \tag{4.4}$$

and define $c^2 \equiv \sum_j c_j^2$. In Table 4 we give the corresponding expressions for the radii $r_i = (\boldsymbol{r}_i \cdot \boldsymbol{r}_i)^{1/2}$, the interparticle distances, $r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j|$, the cosines $\gamma_{ij} = \boldsymbol{r}_i \cdot \boldsymbol{r}_j / r_i r_j$, and other pertinent geometrical quantities, including the Gramian determinant Γ and its principal minors $\Gamma^{(i)}$. The scaled centrifugal potential, $U' = f^{-1} U$, thus is given by:

$$U' = \frac{1}{2(a+a')b^2}\left[\frac{a'^2+b^2}{m_1} + \frac{a^2+b^2}{m_2} + \frac{(a+a')^2}{m_3}\right] + \frac{1}{2(a+a')c^2}\left(\frac{a'^2}{m_1} + \frac{a^2}{m_2}\right). \tag{4.5}$$

The scaled Coulomb potential is given by:

$$V' = \frac{Z_1 Z_2}{a+a'} + \frac{Z_2 Z_3}{(a'^2+b'^2)^{1/2}} + \frac{Z_3 Z_1}{(a^2+b^2)^{1/2}}. \tag{4.6}$$

The global minimum of $W = U' + V'$ occurs when $c \to \infty$, and in this limit:

$$U' = \frac{1}{8A^2}\left(\frac{r_{23}^2}{m_1} + \frac{r_{31}^2}{m_2} + \frac{r_{12}^2}{m_3}\right), \tag{4.7}$$

where A is the area of the triangle formed by the three particles, $A = (a+a')b/2$. This result can be written in a more perspicuous form:

$$U' = \sum_{i=1}^{N} \frac{1}{2m_i h_i^2}, \tag{4.8}$$

in terms of the quantities $h_i \equiv 2A/r_{jk}$. These specify the perpendicular distances from the three vertices of the triangle to the opposite sides or their extensions.

Table 4. Geometrical quantities for three-particle system

Quantity	$i = 1, ij = 12$	$i = 2, ij = 23$	$i = 3, ij = 31$
r_i	$(a^2 + c^2)^{1/2}$	$(a'^2 + c^2)^{1/2}$	$(b^2 + c^2)^{1/2}$
r_{ij}	$a + a'$	$(a'^2 + b^2)^{1/2}$	$(a^2 + b^2)^{1/2}$
γ_{ij}	$(c^2 - a'a)/(r_1 r_2)$	$c^2/(r_2 r_3)$	$c^2/(r_3 r_1)$
$\Gamma^{(i)}$	$(a'^2 b^2 + r_{23}^2 c^2)/(r_2^2 r_3^2)$	$(a^2 b^2 + r_{31}^2 c^2)/(r_3^2 r_1^2)$	$r_{12}^2 c^2/(r_1^2 r_2^2)$
h_i	$2A/r_{23}$	$2A/r_{13}$	$2A/r_{12}$
	$\Gamma = \frac{(a+a')^2 b^2 c^2}{r_1^2 r_2^2 r_3^2}$		
	$A = \frac{1}{2}(a+a')b = [s(s - r_{12})(s - r_{23})(s - r_{31})]^{1/2}$		
	$s = \frac{1}{2}(r_{12} + r_{23} + r_{31})$		

Finally, we obtain the effective potential in a compact form:

$$W = \sum_{i=1}^{N} \left(\frac{1}{2m_i h_i^2} + \sum_{j=i+1}^{N} \frac{Z_i Z_j}{r_{ij}} \right). \tag{4.9}$$

This is independent of the location of the origin, as expected. Likewise, W is unchanged if the signs of all three nuclear charges are reversed.

Table 5 gives the Lewis structures and energies ϵ_∞ obtained by minimizing W for several three-particle systems. These include helium with the nucleus fixed ($N = 2$) and without the nucleus fixed ($N = 3$), and with one or both electrons replaced by μ^- mesons. Also shown is an artificial hydride ion, with nuclear charge $Z_3 = 1.2$, to illustrate the phenomenon of "symmetry breaking". Even for systems in which two of the particles are identical, the global minimum is not always a symmetrical Lewis structure [1, 12]. For a two-electron atom with $Z \geqslant 2$ the effective potential W has a single minimum with isosceles symmetry, but as Z is reduced a pair of unsymmetrical local minima appear, and the isosceles configuration eventually develops into a saddle point [12]. Similarly, for the hydrogen molecule ion W has isosceles symmetry when the internuclear distance is small, but as it increases W develops a double minimum with the electron closer to one or the other nucleus [13].

The examples of Table 5 illustrate some recurrent features. Removing the approximation of a fixed nucleus causes the Lewis structure to expand slightly and to become slightly less stable; we show the percentage changes in parentheses. For He, the energy ϵ_∞ shifts upwards by ~0.015%. This result, from the very simple $D \to \infty$ limit, agrees extremely well with computations [14] of the effect of finite nuclear mass for $D = 3$, which find an energy shift of ~0.014% in the same direction. These effects are amplified for muonic atoms. When both electrons in helium are replaced by negative muons, the size of the atom shrinks, approximately in the mass ratio m_μ/m_e; however, when this factor is scaled out from both distance and energy, the changes are small; the scaled Lewis structure for

Table 5. Lewis structures for three-particle systems

E.g.	$Z_1/Z_2/Z_3$	$m_1/m_2/m_3$	$\bar{r}_{12}/\bar{r}_{23}/\bar{r}_{31}$	$\epsilon_\infty/(m_2 Z_3^2)$
	-1	m_e	0.8971494	-0.6844423
($N = 2$)	-1	m_e	0.6069637	
	$+2$	∞	0.6069637	
	-1	m_e	0.8972544 (+0.012%)	-0.6843398
($N = 3$)	-1	m_e	0.6070512 (+0.014%)	(-0.015%)
	$+2$	m_α	0.6070512 (+0.014%)	
$\alpha\mu\mu$	-1	m_μ	0.004443249 (+2.35%)	-0.6639983
	$-$	m_μ	0.003022489 (+2.87%)	(+2.99%)
	$+2$	m_α	0.003022489 (+2.87%)	
$\alpha\mu e$	-1	m_e	1.000127 (+0.013%)	-0.4868255
	-1	m_μ	0.00248669 (+2.87%)	(-2.83%)
	$+2$	m_α	1.000124 (+0.012%)	
"H^-"	-1	m_e	3.201014 (+0.16%)	-0.5175762
	-1	m_e	0.8520228 (+0.045%)	(-0.056%)
	$+1.2$	m_p	3.040966 (+0.17%)	

$m_e = 1$; $m_\mu = 206.7686$; $m_p = 1836.154$; $m_\alpha = 7296.294$

the dimuonic atom is less stable and more expanded than ordinary helium by about 2.9%. When one electron in helium is replaced by a negative muon, we find the Lewis structure minimum gives an energy $\epsilon_\infty = -402.6409$ hartrees, in excellent agreement with a 35-term variational calculation for $D = 3$, which obtained -402.641014 hartrees [15]. As shown in Appendix B, this close agreement arises from the large mass disparity between the electron and muon, which allows a very accurate hydrogenic approximation.

4.2. *Many-electron Langmuir vibrations*

The key question for dimensional scaling is how to connect the readily solvable $D \to \infty$ limit to the physical problem at $D = 3$. Here we illustrate some aspects for a many-electron atom from the perspective of the $1/D$ perturbation expansion [1–5]. In this approach the scaled energy $\epsilon = fE$ is evaluated as a power series:

$$\epsilon_D = \sum_{n=0}^{\infty} \epsilon^{(n)} D^{-n}. \tag{4.10}$$

In practice, it is expedient to derive the expansion in terms of $f^{-1/2}$ and then recast the result to obtain the $1/D$ series. This corresponds to expanding the wavefunction as:

$$\phi = \sum_{n=1}^{\infty} \phi_n f^{n/4}. \tag{4.11}$$

It is also useful to introduce vibrational coordinates x_i and y_{ij} defined by:

$$r_i = \bar{r}_i(1 + f^{-1/4} x_i) \quad \text{and} \quad \gamma_{ij} = \bar{\gamma}_{ij} + f^{-1/4} y_{ij}. \tag{4.12}$$

These represent dimension-scaled displacements from the Lewis structure. If we then expand all terms in the Schrödinger equation to order $f^{-1/2}$, we obtain [3, 16] an eigenvalue equation for $\epsilon^{(1)}$, the first-order perturbation coefficient:

$$[T\{x_i, y_{ij}\} + W_2\{x_i, y_{ij}\}]\phi_0 = \epsilon^{(1)}\phi_0. \tag{4.13}$$

Here W_2 is a quadratic function of the vibrational displacements. Both T and W_2 have the same form for each of the three Cases of Tables 1–3, and Eq. (4.13) has the standard form for a system of coupled harmonic oscillators, which is separable in terms of normal coordinates. Thus, $\epsilon^{(1)}$ can be determined from the normal mode frequencies and the corresponding Langmuir vibrational modes can be obtained from the normal coordinate transformation by means of the FG matrix method [8]. The higher order perturbation coefficients $\epsilon^{(n)}$ can then be calculated from a recursive algorithm [5, 17]. The energy expansion of Eq. (4.10) is in general a divergent asymptotic series, but summation techniques can give very accurate results [5]. The method appears feasible for many-electron atoms and molecules.

If the energy expansion is simply truncated at first order and then augmented by an appropriate summation procedure, then the results for the N-electron atom are comparable in accuracy to a Hartree–Fock calculation [4]. However, the qualitative picture of harmonic Langmuir vibrations that the first-order expansion represents is an entirely different model from the independent particle scheme invoked for the Hartree–Fock approximation. The large-D limit explicitly displays collective strongly correlated motions of all the particles, whereas the Hartree–Fock approximation averages over these collective motions in order to weaken the correlations.

The form of the Langmuir vibrations offers insight into the particle correlations even at $D = 3$. The vibrational normal modes correspond to approximate symmetries of the Hamiltonian that become exact in the $D \to \infty$ limit. To illustrate this, we consider an N-electron atom with fixed nucleus. Loeser [4] has shown that the Lewis structure for a neutral atom with $Z < 15$, or for any atomic cation, is an N-dimensional simplex specified by just two parameters: $\bar{r} = r_i$ and $\bar{\gamma} = \gamma_{ij}$, for all i and j. The vibrations of the simplex can be described in terms of $\tau = N(N+1)/2$ orthogonal normal coordinates. In general, there are five distinct normal modes, which belong to three different irreducible representations of the point group of the simplex, the symmetric group S_N. Two nondegenerate modes belong to the totally symmetric representation A_1. The normal coordinates for these modes can be constructed [8] as linear combinations of symmetry-adapted internal coordinates, a symmetric stretch x and a symmetric bend y defined as:

$$x = N^{-1/2} \sum_{i=1}^{N} x_i \tag{4.14}$$

and

$$y = [N(N-1)/2]^{-1/2} \sum_{i=1}^{N} \sum_{j=i+1}^{N} y_{ij}. \tag{4.15}$$

Since x and y can serve as a basis for the A_1 representation, the harmonic portion of the effective potential can be written in the form:

$$W_2 = f_{xx}x^2 + 2f_{xy}xy + f_{yy}y^2 + W_{rest}, \tag{4.16}$$

where W_{rest} is independent of x and y. If the coupling constant f_{xy} is small compared to f_{xx} and f_{yy}, as happens for two-electron atoms [3, 16], then x and y are approximate normal coordinates and the harmonic wavefunction is approximately separable in terms of them.

This situation is pertinent to a long-standing question associated with the "adiabatic approximation" often employed in applications of hyperspherical coordinates to atomic structure [18]. This assumes that the dependence of the wavefunction on the hyperspherical radius R is approximately separable, where:

$$R = \left(\sum_{i=1}^{N} r_i^2 \right)^{1/2}. \tag{4.17}$$

For two-electron atoms, computational evidence for this approximate separability was provided in 1968 by Macek [19]. The physical reason remained unclear, although it was later suggested that it is due to some unidentified hidden symmetry [20]. A recent analysis of the two-electron case [16] inferred that this hidden symmetry is in fact the point group of the Lewis structure. The argument is quite direct. Using Eq. (4.12), we expand the hyperspherical radius to first order in $D^{-1/2}$. For the symmetric Lewis structure:

$$\begin{aligned} R &\sim 2^{1/2}\bar{r}[1 + 2^{-1/2}D^{-1/2}(x_1 + x_2)] \\ &= 2^{1/2}\bar{r}(1 + D^{-1/2}x). \end{aligned} \tag{4.18}$$

Therefore, the approximate separability of the Langmuir vibrations in terms of the symmetric stretch x implies approximate separability in terms of R. Here we note that the second equality in Eq. (4.18) holds for arbitrary N. This suggests that the approximate separability with respect to R will obtain for any atom for which the Lewis structure is a simplex.

5. Discussion

Virtually all pragmatic electronic structure calculations for the "real world" with $D = 3$ employ the Rayleigh–Ritz variational method; a vast methodology has been built up and encoded for computers. Dimensional scaling treatments have so far used almost solely $1/D$ perturbation expansions, however, with the exception of a few calculations for two-electron atoms [21, 22]. The new version of the D dimensional Schrödinger equation, designated here as Case (ii), facilitates combining D scaling with variational techniques and computer codes.

In addition to augmenting the Hamiltonian with the centrifugal potential, according to (2.15), two further ingredients will be required. To exploit the opportunity to connect $D = 3$ results with the exactly solvable large-D regime, we need to use variational trial functions capable of simulating well the D dependence of the true wavefunction. In good part, means to implement this criterion will have to be explored empirically. We also need to find better scaling procedures. Without scaling, the addition of the D-dependent centrifugal potential makes the electronic energy vanish as $D \to \infty$. The scaling transformation, in the form of Eq. (4.1), is equivalent to taking the ratio to a hydrogenic atom at the same D value; this renders the large-D limit finite and thereby permits dimensional interpolation. An ideal strategy would be to transform to some quantity that is independent or nearly independent of D. Again, the search for a generic D dependence that could be used to improve the scaling scheme will have to be pursued empirically. Use of variational methods will greatly aid this search.

The generalized formulation developed in this paper may find other inviting applications in treatments that augment [23, 24], abandon [25], or seemingly invert [26] the Born–Oppenheimer approximation. Useful as it is, the traditional view that in molecules the nuclei are localized with a definite geometric structure is only a limiting case. With sufficient vibrational excitation, the molecular structure undergoes a "melting" transition [27], the definite geometry disappears, and the molecular point group is no longer valid for predicting degeneracies. In such straits, the only valid symmetry group is that intrinsic to the Hamiltonian, the Longuet–Higgens group [28]. Likewise, the traditional view of electrons as diffuse, structureless clouds is just a limiting case. Particularly in two-electron excited states, striking evidence of pseudomolecular behavior appears, in which the electrons exhibit collective rotational and vibrational modes [29–31]. Over a wide range, the interelectronic distance indeed can serve as an adiabatic coordinate, entirely analogous to the internuclear bond of a molecule [26]. These qualitative changes with the level of internal excitation are heuristically similar to the transition between hyperquantum and pseudoclassical character in scanning from the low-D to the high-D limit [1–3]. The Lewis structure and Langmuir vibrations have indeed proven useful in interpreting collective modes of excited two-electron atoms [31]. Similar analysis can now be pursued for many-electron modes.

Although electronic correlation has motivated our study of dimensional scaling, the general expressions obtained in Eqs. (3.18)–(3.22) for the kinetic energy, centrifugal potential, and Jacobian weighting function are applicable to the S states of any many-body Schrödinger equation.

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Appendix A: The Gramian determinant

If a set ($i = 1, 2, \ldots, N$) of unit vectors $\boldsymbol{x}_i$ in a Euclidean space is linearly dependent, then there exists a set of numbers, not all of which are zero, such that:

$$c_1\boldsymbol{x}_1 + c_2\boldsymbol{x}_2 + \cdots + c_N\boldsymbol{x}_N = 0. \tag{A1}$$

Taking the scalar product of this equation with each of the vectors in turn, we obtain the set of equations:

$$\begin{aligned} c_1\gamma_{11} + c_2\gamma_{12} + \cdots + c_N\gamma_{1N} &= 0, \\ c_1\gamma_{21} + c_2\gamma_{22} + \cdots + c_N\gamma_{2N} &= 0, \\ &\vdots \\ c_1\gamma_{N1} + c_2\gamma_{N2} + \cdots + c_N\gamma_{NN} &= 0, \end{aligned} \tag{A2}$$

where $\gamma_{ij} \equiv \boldsymbol{x}_i \cdot \boldsymbol{x}_j$. The *Gramian determinant* [7] is defined as:

$$\Gamma \equiv |\gamma_{ij}| \tag{A3}$$

and Eqs. (A2) have a non-trivial solution for the c_i if $\Gamma = 0$. Thus, the vectors are linearly dependent if and only if the Gramian determinant is zero.

Here we derive properties of Γ required to evaluate Eq. (3.17) of the text. Let C_{ij} denote the cofactor of the element γ_{ij} in Γ, that is, $(-1)^{i+j}$ multiplied by the determinant of the matrix obtained by deleting the ith row and the jth column. Then, expanding Γ in terms of the cofactors, we obtain:

$$\Gamma = \sum_{j=1}^{N} \gamma_{ij}C_{ij} = \sum_{j=1}^{N} \gamma_{ij}C_{ji}, \tag{A4}$$

so that

$$\frac{\partial \Gamma}{\partial \gamma_{ij}} = C_{ij} + C_{ji}. \tag{A5}$$

From these relations and from the fact that $\gamma_{ii} = 1$, it follows that:

$$\Gamma - \tfrac{1}{2}\sum_{j \neq i}^{N} \gamma_{ij}\frac{\partial \Gamma}{\partial \gamma_{ij}} = \gamma_{ii}C_{ii} = \Gamma^{(i)}, \tag{A6}$$

where $\Gamma^{(i)} \equiv C_{ii}$ is the ith principal minor of Γ. From the theory of determinants, we also know that if $k \neq i$, then:

$$\sum_{j=1}^{N} \gamma_{kj}C_{ij} = 0. \tag{A7}$$

We can use Eqs. (A6) and (A7) to show that:

$$\sum_{k \neq i}^{N} (\gamma_{jk} - \gamma_{ij}\gamma_{ik})\frac{\partial \Gamma}{\partial \gamma_{ik}} = -2\gamma_{ij}\Gamma, \quad \text{for } 1 \leqslant i < j \leqslant N. \tag{A8}$$

From Eq. (A6) it follows that:

$$\sum_{k\neq i}^{N}(\gamma_{jk}-\gamma_{ij}\gamma_{ik})\frac{\partial\Gamma}{\partial\gamma_{ik}}=2\gamma_{ij}[\Gamma^{(i)}-\Gamma]+\sum_{k\neq i}^{N}\gamma_{jk}\frac{\partial\Gamma}{\partial\gamma_{ik}},\tag{A9}$$

while from Eqs. (A4) and (A7) we have:

$$\sum_{k\neq i}^{N}\gamma_{jk}\frac{\partial\Gamma}{\partial\gamma_{ik}}=2\sum_{k\neq i}^{N}\gamma_{jk}C_{ik}=-2\gamma_{ij}\Gamma^{(i)}.\tag{A10}$$

Combining these results yields the desired relation, Eq. (A8).

We can now readily evaluate the four sums in Eq. (3.17) involving derivatives of Γ. The quantity denoted S_{ik} is obtained directly from Eq. (A8); on relabeling the summation index, the term containing S_{ik} is then incorporated into the coefficient of $\partial\phi/\partial\gamma_{ij}$ in the kinetic energy. Likewise, the quantity S'_i is obtained from Eq. (A6), which yields:

$$S'_i\equiv\Gamma^{-1}\sum_{j\neq i}^{N}\gamma_{ij}\frac{\partial\Gamma}{\partial\gamma_{ij}}=2\left[1-\frac{\Gamma^{(i)}}{\Gamma}\right].\tag{A11}$$

The quantity S''_i is evaluated by successive application of Eqs. (A8) and (A6), which gives:

$$\begin{aligned}S''_i&\equiv\Gamma^{-2}\sum_{j\neq i}^{N}\sum_{k\neq i}^{N}(\gamma_{jk}-\gamma_{ij}\gamma_{ik})\frac{\partial\Gamma}{\partial\gamma_{ij}}\frac{\partial\Gamma}{\partial\gamma_{ik}}\\&=-2\Gamma^{-1}\sum_{k\neq i}^{N}\gamma_{ik}\frac{\partial\Gamma}{\partial\gamma_{ik}}=-2S'_i=-4\left[1-\frac{\Gamma^{(i)}}{\Gamma}\right].\end{aligned}\tag{A12}$$

Finally, the quantity S'''_i can be recast as:

$$\begin{aligned}S'''_i&\equiv\Gamma^{-1}\sum_{j\neq i}^{N}\sum_{k\neq i}^{N}(\gamma_{jk}-\gamma_{ij}\gamma_{ik})\frac{\partial^2\Gamma}{\partial\gamma_{ij}\,\partial\gamma_{ik}}\\&=\Gamma^{-1}\sum_{k\neq i}^{N}\left\{\frac{\partial}{\partial\gamma_{ik}}\left[\sum_{j\neq i}^{N}(\gamma_{jk}-\gamma_{ij}\gamma_{ik})\frac{\partial\Gamma}{\partial\gamma_{ij}}\right]-\sum_{j\neq i}^{N}\frac{\partial\Gamma}{\partial\gamma_{ij}}\frac{\partial}{\partial\gamma_{ij}}(\gamma_{jk}-\gamma_{ij}\gamma_{ik})\right\},\end{aligned}\tag{A13}$$

and with Eqs. (A8) and (A6) this gives:

$$\begin{aligned}S'''_i&=\Gamma^{-1}\sum_{k\neq i}^{N}\left[\frac{\partial}{\partial\gamma_{ik}}(-2\gamma_{ik}\Gamma)+\gamma_{ik}\frac{\partial\Gamma}{\partial\gamma_{ik}}+\sum_{j\neq i}^{N}\gamma_{ij}\frac{\partial\Gamma}{\partial\gamma_{ij}}\right]\\&=\Gamma^{-1}\sum_{k\neq i}^{N}\left[-2\Gamma-\gamma_{ik}\frac{\partial\Gamma}{\partial\gamma_{ik}}+2(\Gamma-\Gamma^{(i)})\right]\\&=-2+(4-2N)\frac{\Gamma^{(i)}}{\Gamma}.\end{aligned}\tag{A14}$$

The Gramian determinant, Γ, and the principal minor, $\Gamma^{(i)}$, can be used to construct the projection of a vector $\boldsymbol{x}_i$ onto the subspace S spanned by all the other vectors in the set. We illustrate this construction with an example: Suppose that $N=3$ and we wish to construct the projection of $\boldsymbol{x}_3$ onto the subspace spanned by $\boldsymbol{x}_1$ and $\boldsymbol{x}_2$. Let $\boldsymbol{x}_s$ be the projection onto S and $\boldsymbol{x}_n$ the component of $\boldsymbol{x}_3$ normal to S. Then we can write:

$$\boldsymbol{x}_3=\boldsymbol{x}_n+\boldsymbol{x}_s.\tag{A15}$$

Let

$$\boldsymbol{x}_s = a_1\boldsymbol{x}_1 + a_2\boldsymbol{x}_2. \tag{A16}$$

Then the coefficients a_1 and a_2 must simultaneously satisfy the three equations:

$$\begin{aligned} -\boldsymbol{x}_s + a_1\boldsymbol{x}_1 + a_2\boldsymbol{x}_2 &= 0,\\ \boldsymbol{x}_1 \cdot (-\boldsymbol{x}_3 + a_1\boldsymbol{x}_1 + a_2\boldsymbol{x}_2) &= 0,\\ \boldsymbol{x}_2 \cdot (-\boldsymbol{x}_3 + a_1\boldsymbol{x}_1 + a_2\boldsymbol{x}_2) &= 0, \end{aligned} \tag{A17}$$

which can be rewritten in the form:

$$\begin{aligned} a_1\boldsymbol{x}_1 + a_2\boldsymbol{x}_2 + (-1)\boldsymbol{x}_s &= 0,\\ a_1\gamma_{11} + a_2\gamma_{12} + (-1)\gamma_{13} &= 0,\\ a_1\gamma_{12} + a_2\gamma_{22} + (-1)\gamma_{13} &= 0. \end{aligned} \tag{A18}$$

This set of equations will have a solution, $a_1, a_2, (-1)$, if and only if:

$$\begin{vmatrix} \boldsymbol{x}_1 & \boldsymbol{x}_2 & \boldsymbol{x}_s \\ \gamma_{11} & \gamma_{12} & \gamma_{13} \\ \gamma_{12} & \gamma_{22} & \gamma_{23} \end{vmatrix} = 0. \tag{A19}$$

Expanding this determinant in terms of the cofactors of the top row, we obtain:

$$\boldsymbol{x}_s = -\frac{1}{\Gamma^{(3)}} \begin{vmatrix} \boldsymbol{x}_1 & \boldsymbol{x}_2 & 0 \\ \gamma_{11} & \gamma_{12} & \gamma_{13} \\ \gamma_{12} & \gamma_{22} & \gamma_{23} \end{vmatrix}, \tag{A20}$$

and

$$\boldsymbol{x}_n = \boldsymbol{x}_3 - \boldsymbol{x}_s = \frac{1}{\Gamma^{(3)}} \begin{vmatrix} \boldsymbol{x}_1 & \boldsymbol{x}_2 & \boldsymbol{x}_3 \\ \gamma_{11} & \gamma_{12} & \gamma_{13} \\ \gamma_{12} & \gamma_{22} & \gamma_{23} \end{vmatrix} = \frac{1}{\Gamma^{(3)}} \begin{vmatrix} \gamma_{11} & \gamma_{12} & \gamma_{13} \\ \gamma_{12} & \gamma_{22} & \gamma_{23} \\ \boldsymbol{x}_1 & \boldsymbol{x}_2 & \boldsymbol{x}_3 \end{vmatrix}. \tag{A21}$$

Thus:

$$\boldsymbol{x}_n \cdot \boldsymbol{x}_n = \boldsymbol{x}_3 \cdot \boldsymbol{x}_n = \Gamma/\Gamma^{(3)}. \tag{A22}$$

More generally, even if the vectors $\boldsymbol{x}_1, \boldsymbol{x}_2, \boldsymbol{x}_3, \ldots, \boldsymbol{x}_N$ are not unit vectors, we still decompose the vector $\boldsymbol{x}_i$ into a projection onto the subspace spanned by all the other vectors, and a component $\boldsymbol{x}_n$ that is perpendicular to the subspace:

$$\boldsymbol{x}_i = \boldsymbol{x}_s + \boldsymbol{x}_n. \tag{A23}$$

In the general case the square of the length of the perpendicular component is given by:

$$\boldsymbol{x}_n \cdot \boldsymbol{x}_n = R_i^2\,\Gamma/\Gamma^{(i)}, \tag{A24}$$

where R_i is the length of the vector $\boldsymbol{x}_i$ and Γ is the Gramian determinant formed from $\gamma_{ij} \equiv \boldsymbol{x}_i \cdot \boldsymbol{x}_j / R_i R_j$.

Appendix B: Muonic helium atom

When one electron in helium is replaced by a negative muon, the system can be well approximated as separable, since the heavier muon will reside much closer to the nucleus than will the electron. Here we exploit this feature to obtain a simple but very accurate approximation from the Lewis structure. The ground-state energy thus found for the $D \to \infty$ limit proves to be in excellent agreement with that for $D = 3$ from extensive variational calculations [15]. From Eq. (4.9), the effective potential is

$$W = \frac{1}{8A^2}\left(\frac{a^2}{m_1} + \frac{b^2}{m_2} + \frac{c^2}{m_3}\right) + \frac{1}{c} - \frac{Z}{a} - \frac{Z}{b}, \tag{B1}$$

where the interparticle distances are denoted by $a = r_{\alpha\mu}$, $b = r_{\alpha e}$ and $c = r_{\mu e}$, and $Z = 2$ is the nuclear charge. Since $a \ll b$, the correlation between the muon and electron motions will be weak. Accordingly, as in the $D \to \infty$ limit for a Hartree–Fock wavefunction [16], the Jacobian factor will cause the limiting angle between the $\boldsymbol{a}$ and $\boldsymbol{b}$ vectors to be 90°, so we take $c^2 \approx a^2 + b^2$. This gives:

$$W = \frac{1}{2}\left(\frac{1}{M_\mu a^2} + \frac{1}{M_e b^2}\right) - \frac{Z}{a} - \frac{(Z-1)}{b}, \tag{B2}$$

with M_μ and M_e the reduced masses of the muon and electron, respectively, with respect to the nucleus, and with terms of order $(a/b)^3$ and higher omitted. Now W describes two separable, hydrogenic systems: one is the muon interacting with the bare nucleus (an alpha particle), the other the electron interacting with the dressed nucleus, quite effectively screened by the muon. From $\partial W/\partial a = 0$ and $\partial W/\partial b = 0$ we find the particle locations at the minimum:

$$a_m = \frac{1}{ZM_\mu} \quad \text{and} \quad b_m = \frac{1}{(Z-1)M_e}, \tag{B3}$$

and the energy:

$$\epsilon_\infty = W_m = -\tfrac{1}{2}Z^2 M_\mu - \tfrac{1}{2}(Z-1)^2 M_e. \tag{B4}$$

Using the mass values cited in Table 5, we obtain:

$$\begin{aligned} a_m &= 0.002486691 \ (0.002418162), \\ b_m &= 1.000137 \ (1.0), \\ c_m &= 1.000140 \ (1.000003), \\ W_m &= -402.6409 \ (-414.0372), \end{aligned} \tag{B5}$$

where the quantities in parentheses pertain to a fixed nucleus ($m_\alpha = \infty$).

Direct numerical minimization of Eq. (B1), without the approximations introduced in Eq. (B2), yields the same values of a_m and W_m as found in Eq. (B5) to seven figures (the accuracy of the input masses). However, evaluation of b_m and c_m from direct numerical minimization [32] encounters an intrinsic difficulty. The values of W_m and a_m are quite insensitive to b_m and c_m. As seen in Eq. (B4), the major b dependence contributes only ~0.1% to the value of W_m. Also, the smallness of a_m makes $b_m \approx c_m$, as noted above. To resolve this difficulty, we evaluated b_m and c_m by minimizing $W(a_m, b, c)$ instead of $W(a, b, c)$ and obtained:

$$\begin{aligned} b_m &= 1.000124 \ (1.0), \\ c_m &= 1.000127 \ (1.000003). \end{aligned} \tag{B6}$$

The corresponding angle between the muon and electron radii in the Lewis structure:

$$\theta_m = \arccos[\tfrac{1}{2}(a_m^2 + b_m^2 - c_m^2)/a_m b_m], \tag{B7}$$

is 89.9965°, very close to 90°. This illustrates the weakness of the muon-electron correlation, in contrast to the electron-electron correlation in ordinary helium, which has $\theta_m = 95.3°$.

The value of W_m for the $D \to \infty$ Lewis structure of Eq. (B5) is the same to six figures as the energy for $D = 3$ obtained from variational calculations [15]. This is a consequence of the feeble correlation in the muonic atom, which, as seen in Eq. (B4), renders it quasihydrogenic. In such a case, knowledge of the $D \to \infty$ limit determines the energy at $D = 3$ as well, because the dimensional scaling procedure is designed to give exact results for hydrogenic atoms [3]. Likewise, the weakness of the muon-electron correlation is the reason the energy computed with a 1-term variational trial function (-402.641012) is nearly as good as that obtained with a 35-term function (-402.641014).

The agreement between W_m from Eq. (B5) and the variational results can be shown analytically for the 1-term function. This consists of the product of 1*s* orbitals, proportional to $\exp(-\zeta_\mu r_{\alpha\mu}) \exp(-\zeta_e r_{\alpha e})$, with ζ_μ and ζ_e the variational parameters. By expanding the expression obtained by Huang [15] for the energy expectation value, we find that it becomes the same as our Eq. (B2) if we neglect terms of order $(\zeta_\mu/\zeta_e)^3$, which are very small, and replace a with $1/\zeta_\mu$ and b with $1/\zeta_e$. Thus, the minimization of W to obtain the $D \to \infty$ limit is practically equivalent to such a simple variational or Hartree–Fock approximation for $D = 3$ as long as the correlation is very weak. This equivalence no longer holds when the correlation becomes strong.

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