Solution of the Hartree–Fock equations by a pseudospectral method: Application to diatomic molecules

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An improved version of the pseudospectral method is used to accurately solve the Hartree–Fock equations for the neon atom and the diatomic molecules H_2 and Li_2. Because the method eliminates two-electron integrals and is amenable to efficient vectorization on a supercomputer, order of magnitude reductions in computation time can be expected for large polyatomic molecules (for which a straightforward generalization of the procedure described here exists). The present work demonstrates that accuracy comparable to conventional methods can be achieved by the pseudospectral technique.

I. INTRODUCTION

In a previous paper,[1] the Hartree–Fock equations for the neon atom were solved using a pseudospectral method.[5–8] This approach, adapted from hydrodynamic simulations of wall-bounded flows[20–22] and turbulence[19,23] (and recently applied to quantum scattering problems),[2,3] eliminates the need to compute two-electron integrals, scales like N^3 rather than N^4 (where N is the basis set size), and is amenable to efficient vectorization on supercomputers. Hence, provided sufficient accuracy can be obtained, order of magnitude reductions in computation time and storage space (as compared to conventional methods) for polyatomic molecules can be expected.

In this paper, several numerical improvements are introduced which yield stable and accurate results for all cases studied to date. The most important of these is the use of dealiasing,[5–8] a standard technique for removing certain types of errors from a pseudospectral code. Other modifications include an improved eigenvalue solver which enforces orbital orthogonality, a linear least-squares approach to ensure stability of the collocation matrix, and use of the spectral one-electron operator.

In addition to refining the neon results, the diatomic molecules H_2 and Li_2 are investigated. Three-center, one-electron integrals (the only difficult integrals required, even for the polyatomic systems) are evaluated by a one-center expansion method which employs Chebyshev polynomials. While Slater functions are utilized in these calculations, the integral package can handle arbitrary (including numerical) basis functions with no increase in computation time or loss of accuracy.

The dealiasing procedure is designed to make the pseudospectral calculation equivalent to a purely spectral (i.e., conventional Roothaan[10]) one. The results reported here demonstrate that this is the case; potential curves as a function of internuclear separation are computed and compared with standard results for the same basis set. For reasonably designed collocation grids, total energies are within 0.0005 hartree of the spectral results (which, it should be recalled, are not exact solutions either). Furthermore, these results

are relatively insensitive to the precise placement of grid points. While several general principles are developed for grid design, optimization procedures will be reported elsewhere.[13]

Timing results are unsurprising, but comparisons are not emphasized here (note that spectral methods are most efficient for diatomics, where only two-center integrals are required). We are presently developing a vectorized polyatomic version of the pseudospectral code and integral package described below, to be run on a Cray X-MP.[12] Efficiency of the pseudospectral appoach will be best judged by the results obtained from this program. This principal goal of this paper is to demonstrate that the method is capable of sufficient accuracy for chemical applications.

II. PSEUDOSPECTRAL METHOD FOR THE HARTREE–FOCK EQUATIONS

A version of the pseudospectral Hartree–Fock equations was derived in Ref. 1. In this paper, a somewhat different formulation will be used.

A brief review of the underlying principles of the pseudospectral approach will be presented first. The solution to the equations under study appears in two representations: spectral (i.e., as coefficients of a basis set) and physical (i.e., as a set of values of the solution on a grid of points in three-dimensional space). The collocation method[17] is used to transform between representations.

The nature of the quantum chemical electronic structure problem requires considerable modification of the standard hydrodynamic methods, which are principally utilized for regular geometries. However, the crucial factor that enhances computation speed, which is to do one nonlinear multiplication in physical space rather than a spectral convolution, is preserved. More discussion of this point can be found in Ref. 1.

Numerical implementation of the pseudospectral approach requires specification of the precise forms of the operators comprising the Fock operator F. The final calculation consists, as in standard techniques, of iterating the pseudoeigenvalue equations

$$F[\phi] \cdot \phi_i = \epsilon_i \phi_i , \tag{1}$$

where the ϕ_i can be represented either in spectral or physical space. In Ref. 1, a physical space formulation was used. The improvements described below mandate that the ultimate representation be a spectral one; the physical space vectors are used in intermediate calculations required in the assembly of F.

A. Construction of the Fock operator in spectral space

The one-electron operator

$$H_0 = -\frac{1}{2}\nabla^2 - \sum_N \frac{Z_N}{|\mathbf{r} - \mathbf{r}_N|} \qquad (2)$$

will be represented by the usual basis set matrix, i.e.,

$$[\mathbf{H}_0]_{ij} = \langle \phi_i |H_0| \phi_j \rangle ,$$

where the $\{\phi_k\}$ are a standard quantum chemical basis set of N atomic orbitals. This smooths errors at the nuclei and costs no computation time, as the spectral $\mathbf{H}_0$ matrix is required to evaluate the total energy in any case. The collocation matrices $\mathbf{R}$ and $\mathbf{R}^{-1}$, defined by $[\mathbf{R}]_{ij} = \phi_j(r_i)$, where the $\{r_k\}$ are a set of N grid points, are used to construct the Coulomb and exchange operators as in Ref. 1, but the final matrix equation is ultimately in spectral, rather than physical, space. For example, the spectral Coulomb operator $\mathbf{J}_{sp}$ is

$$\mathbf{J}_{sp} = \mathbf{R}^{-1} \mathbf{J}_{ph} \mathbf{R} . \qquad (3)$$

$\mathbf{R}$ takes the spectral vector $\mathbf{c}$ into physical space, $\mathbf{J}_{ph}$ is the diagonal physical space Coulomb operator defined in Eq. (10) of Ref. 4, and $\mathbf{R}^{-1}$ returns to spectral space. The exchange operator is transformed in a similar fashion. Canonical orthogonalization[16] is used to eliminate the overlap matrix on the right-hand side of the spectral Hartree–Fock equations, and canonical functions with small eigenvalues are discarded as in standard procedures.

The important aspects of the pseudospectral approach are

(1) In each of the nonlinear terms (Coulomb and exchange) a convolution in spectral space mandated by the Roothaan procedure is replaced by a multiplication in physical space. This eliminates two-electron integrals, leads to $O(N^3)$ computation time scaling and integral storage requirements, and allows straightforward vectorization of Fock matrix assembly.

(2) The price to be paid for this is the approximation entailed in constructing the spectral vector $\mathbf{c}$ via $\mathbf{R}^{-1}$ from physical space on a relatively sparse grid (a large number of points could be used, of course, but this would increase computation times). As long as the basis set is highly accurate, this step leads to small errors. For smaller basis sets, however, undesirable dependence of the results on the collocation grid can result. In the next two sections, useful modifications of the pseudospectral technique are described which will remedy this problem at minimal cost. Substantial gains in accuracy with respect to earlier work are obtained.

It should be noted that the above approach is similar in spirit to the discrete variable representation (DVR) of Light and co-workers.[24] More specifically, Eq. (3) is analogous to Eq. (2.17) of Ref. 24, with $\mathbf{J}$ replaced by a linear external

potential matrix $\mathbf{V}$. The DVR can in fact be considered a particular formulation of the pseudospectral approach, and results should be transferable between the two formalisms.

B. Dealiasing

The concept of dealiasing is best understood in spectral space. Consider a spectral vector

$$\mathbf{c} = \begin{bmatrix} c_1 \\ \cdot \\ \cdot \\ c_N \end{bmatrix}$$

acted on by an operator (either linear or nonlinear) $\hat{O}$. The exact action of $\hat{O}$ on $\mathbf{c}$ is given by

$$\hat{O}\mathbf{c} = \hat{O}\left\{ \sum c_j \phi_j \right\}$$

$$= \sum c_j \hat{O}\phi_j . \qquad (4)$$

If the operation $\hat{O}\phi_j$ produces *only* functions contained in the original basis set for all ϕ_j, no aliasing terms (components *outside* the basis set) are produced. However, this is not generally the case, especially for basis functions and operators used in quantum chemistry.

For the pseudospectral Coulomb and exchange operators, the operator $\hat{O}$ generates the results of $\hat{O}\phi_j$ in physical space. To return to spectral space, the collocation method is used (see Ref. 1 for simple illustrations in the quantum chemistry context); thus

$$\hat{O}\mathbf{c} = \mathbf{R}^{-1} \mathbf{O}_{ps} \mathbf{c} , \qquad (5)$$

where $\mathbf{O}_{ps}$ produces a vector in physical space, and $\mathbf{R}^{-1}$ is the collocation matrix defined above.

If $\mathbf{O}_{ps}\mathbf{c}$ contains no aliasing errors, this procedure is exact. If there is aliasing, however, the residual of $\mathbf{O}_{ps}\mathbf{c}$ outside the basis set will be (incorrectly) represented by available basis functions. Several options are possible in dealing with this problem.

One approach is to ignore the entire issue. Many fluid mechanical calculations are carried out this way, and the results are not necessarily worse than for a dealiased code.[5] However, there are some situations in which undesirable consequences of aliasing appear. Numerical results indicate that the present problem is of this type.

A second approach is to project out the alias. Purely spectral methods do this exactly. In hydrodynamic pseudospectral codes, analogous results are obtained by discarding some percentage (typically 1/2) of the basis set coefficients.[8] This results in an exact dealiasing because the Navier–Stokes equations are quadratically nonlinear and the basis sets used are either Fourier modes of Chebyshev polynomials, which yield functions of at most index $2N$ (where N is the label of the largest wave vector in the basis set) from a quadratic multiplication step.

The analogous procedure for the HF equations will not lead to as well defined a result, because the basis functions and operators are more complicated.

However, we can use as dealiasing functions atomic orbitals with large radial or angular quantum numbers, or dif-

ferent exponents than those used in the basis set. Indeed, the optimal choice would be functions which would complete the basis set most rapidly; thus, standard approaches to constructing accurate large quantum chemical basis sets can be employed.

To formalize the procedure, we assume a single symmetry block (extension to more blocks is trivial) in the Fock matrix. The pseudospectral problem is now defined with N basis functions, M dealiasing functions, and $N + M$ grid points. The function matrix $\mathbf{R}$ is then $N \times (N + M)$ (only basis functions are included), but the collocation matrix $\mathbf{R}^{-1}$ is the inverse of the full $(N + M) \times (N + M)$ function matrix. The operator $\mathbf{O}_{ps}$, which takes N basis coefficients to $(N + M)$ grid points, is therefore $(N + M) \times N$. For example, the pseudospectral Coulomb operator $\mathbf{J}_{sp}$ is given by the product of the $N \times (N + M)$ function matrix with the diagonal $(N + M) \times (N \times M)$ physical space Coulomb matrix. The spectral Coulomb operator $\mathbf{J}_{sp}$ becomes

$$\mathbf{J}_{sp} = \mathbf{P}\mathbf{R}^{-1}\mathbf{J}_{ps}$$
$$= \mathbf{P}\mathbf{R}^{-1}\mathbf{J}_{ph}\mathbf{R} . \tag{6}$$

Here $\mathbf{P}$ is a projection operator which removes the dealiasing functions. If these are constructed to be orthogonal to the basis set (e.g., via Schmidt orthogonalization) then $\mathbf{P}$ is the $N \times (N + M)$ matrix

$$\mathbf{P} = [\mathbf{1} \quad \mathbf{0}] ,$$

where $\mathbf{1}, \mathbf{0}$ are $N \times N$ unit and $M \times N$ zero matrices, respectively. The result for $\mathbf{J}_{sp}$ is then an $N \times N$ matrix which is a suitable component for the spectral Fock operator.

The principal computational requirement for dealiasing is generation of the potential integrals

$$A_{nm}(\mathbf{r}_k) = \int \frac{\phi_n(\mathbf{r})\phi_m(\mathbf{r})}{|\mathbf{r} - \mathbf{r}_k|} d^3\mathbf{r} \tag{7}$$

at $N + M$ (rather than N) grid points. Thus, for $M = N$ (i.e., one dealiasing function per basis function), integral computation time would increase by a factor between 1 and 2 (doubling the grid size does *not* necessarily double integral computation time).

This is a worthwhile tradeoff for the improved numerical accuracy obtained. Note that in the limit that the dealiasing procedure becomes exact, the pseudospectral method is variational. Also, increasing the basis set size to $N + M$ would raise integral computation and storage requirements to $(N + M)^3$ rather than to at most $(N + M)N^2$.

It is also necessary to compute the overlap integrals of the basis and dealiasing functions in order to perform the Schmidt orthogonalization. This leads to a negligible increase in computation time.

C. Least–squares method

The collocation method as used in this paper has one substantial difficulty; in the absence of an efficient grid optimization algorithm, instabilities on the order of ± 0.005 hartree in the total energy can be generated by the presence of small eigenvalues in the collocation matrix. These result in the inverse transform $\mathbf{R}^{-1}$ amplifying errors due to incompleteness of the basis set. The problem occurs only in the

largest basis set calculation (on Li_2), and is manifested in that the above energy fluctuations can be produced by small perturbations of the grid. This is clearly undesirable for accurate quantum chemical calculations.

The problem can be remedied by introducing additional grid points and using a linear least-squares (rather than collocation) matrix to transform from physical to spectral space. At the cost of a modest (20%–30%) increase in computation time, stability of the results is enhanced substantially.

The least-squares procedure is implemented by evaluating the basic potential integrals at $N + M + L$ grid points (L is the number of additional points), so as to generate the results of multiplications in the nonlinear terms on this expanded grid. The function matrix $\mathbf{R}$ (including both dealiasing and basis function) is now $(N + M) \times (N + M + L)$; the inverse transform matrix $\mathbf{R}^{-1}$ is computed from the normal least-squares equations,[17] i.e.,

$$\mathbf{R}^{-1} \equiv \mathbf{P}(\mathbf{R}^+\mathbf{R})^{-1}\mathbf{R}^+ . \tag{8}$$

Note that $\mathbf{R}^{-1}$ is now an $N \times (N + M + L)$ matrix (recall that the dealiasing functions are projected out by the projection operator $\mathbf{P}$). This operator is computed as a preprocessing step which consumes negligible computation time; the primary increase comes from the requirement that additional potential integrals be evaluated.

A modification of the above procedure is to weight the grid points in the least-squares fitting procedure differently. This is accomplished with a trivial alteration of Eq. (8), and is used to allow placement of additional points where greater variation of the wave function (but not necessarily larger contributions to the energy) are expected.

D. Implementation of symmetry conditions

As in conventional techniques, the Fock matrix must be factored into separated blocks if basis functions cannot be mixed because of symmetry. This is accomplished simply by setting F_{ij} equal to zero if ϕ_i and ϕ_j are decoupled. Note, however, that the potential integrals A_{nm} [cf. Eq. (7)] must still be evaluated for all pairs of basis functions n and m to compute the nonzero exchange interactions between orbitals of different symmetry.

E. Enforcing orthogonality

The pseudospectral Fock operator is not, in general, symmetric, even after canonical orthogonalization. Hence, there is no guarantee that orbital solutions will be orthogonal, other than in the limit that the basis set becomes exact.

However, orthogonality can be enforced by a deflation procedure in which orbitals are successively removed from the basis set. Suppose the first solution is ψ_0, and we want ψ_1 to satisfy $\langle \psi_1 | \psi_0 \rangle = 0$. We define a new basis set consisting of the $N - 1$ functions

$$\phi'_j = \phi_j - \langle \psi_0 | \phi_j \rangle \psi_0 ,$$

where the function ϕ_k with the maximal projection on ψ_0 is excluded. The new Fock matrix is

$$\widetilde{F}_{ij} = \langle \phi_j' | F | \phi_j' \rangle$$

$$= \langle \phi_j | F | \phi_i \rangle - \langle \psi_0 | F | \phi_j \rangle . \qquad (9)$$

Note that $\langle \psi_0 | F \neq \epsilon_0 \psi_0$ because a non-Hermitian matrix has differing left and right eigenvectors. The new $\widetilde{F}$ must be reorthogonalized by the inverse of the overlap matrix of the $\{\phi_k\}$'s. All of these operations consume relatively little computation time, and readily generalize to an efficient recursive procedure for M occupied orbitals. The lowest eigenvalue of the new Fock matrix is computed by the power method,[17] which is very efficient when a good initial guess is available. Hence, the overall procedure involves ignoring overlap for the first few iterations and employing the IMSL routine EIGRF to diagonalize F, followed by the above procedure to refine the solutions.

F. Numerical integration methods

The principal integral computations required in the pseudospectral method are three-center, one-electron integrals of the form specified by Eq. (7). For this paper, these integrals were evaluated by a numerical integration method using a one-center expansion in Chebyshev and Legendre polynomials. The details of the method will be described in a subsequent paper.[12] Slater basis functions were employed, although the integrator is capable of handling any basis functions (including numerical ones) without an increase in computation times. Integral accuracy was established to be 10^{-6} hartree. Calculation of overlap, kinetic, and nuclear potential energy integrals using the same approach is straightforward, consuming negligible computation time.

III. NUMERICAL RESULTS
A. Grid design, choice of basis set, and dealiasing functions

The purpose of this paper is to demonstrate that reasonable results can be achieved by a pseudospectral approach with minimal effort in grid construction and choice of dealiasing functions. The results reported in the engineering and fluid mechanics literature for grid optimization[4,18] suggest that it will be possible to develop highly accurate, automatic procedures for the present problem. Here, however, grids were constructed using a few simple principles:

(1) Avoidance of regions very close to the nuclei, where the basis set is inaccurate.

(2) Avoidance of small eigenvalues in the collocation matrix, which introduce large numerical errors when $\mathbf{R}^{-1}$ is applied. This requires minimally adequate separation of grid points.

(3) Coverage of the relevant region of physical space (easily deduced from the basis set).

For an atom, only a one-dimensional grid is required; this was obtained simply by associating two grid points with each basis *and dealiasing* function, placing them around the function's maximal density. For the diatomic molecules, each atom "carries" a two-dimensional atomic grid which moves with it as the internuclear separation R increases. This atomic grid is generated from an exponential distribution for each orbital dispersed in an angular pattern which covers the upper half of the $\phi = 0$ plane. In addition, several points are placed in the bonding region and remain fixed as R is varied. For a homonuclear diatomic, only one atomic grid is required, the points of which lie on one side of the mirror plane of symmetry.

The results reported here were obtained from grids generated by using the above guidelines. Perturbation of grid points by 5%–10% produces little change in the total energy or orbital eigenvalues ($\approx \pm 0.0001$ hartree) unless a near singularity is introduced in the collocation matrix. Furthermore, relative energy differences as a function of R appear to be affected even less.

On the other hand, major changes in the grid structure (e.g., significantly different inner or outer radii) can lead to larger variation ($\approx \pm 0.005$ hartree). Thus, automatic optimization procedures will have to be developed for polyatomic molecules. As stated above, this should be attainable, given the success of grid optimization in other disciplines for extremely demanding problems (e.g., shock waves in highly irregular geometries).

Standard quantum chemical basis sets were used for all calculations. Dealiasing functions were chosen so as to possess amplitude and functional variation in the regions of space occupied by the orbital solutions. Again, no effort was made at optimization, and the final results are relatively insensitive (± 0.0001 hartree for 5%–10% variation) to precise choices of exponents. Improvement of the dealiasing basis set (e.g., via conventional Roothaan calculations on small systems, for later use in large problems) will be straightforward

B. Neon atom

We have obtained results for the neon atom using the Slater basis set of Clementi and Roetti[9] with two additional $2p$ functions and a complementary set of dealiasing functions. Each symmetry block has six basis functions and six dealiasing functions. The same 12 radial grid points are used for each block. Exponents for the functions and grid positions are given in Table I.

Orbital eigenvalues and total energy results are presented in Table II. As can be seen, quantitative agreement of the total energy is obtained. No problems arose in achieving convergence of the HF equations, e.g., starting from eigenvectors of the bare one-electron operators.

Differences in orbital eigenvalues are as large as 0.001 hartree (for the ϵ_1 eigenvalue). This can possibly be attributed to the augmentation of the basis set in our calculations with functions whose density peaks near the nucleus. Alternatively, it is not surprising to detect greater variation in the wave function than the total energy for the spectral and pseudospectral procedures. It is by no means clear that a spectral approach provides a more accurate wave function; indeed, by a least-squares criterion, collocation often produces a better fit to a function than complete projection. This issue may be relevant in computing (e.g.) accurate tails of wave functions, as are required in electron transfer calculations.

Similar effects are evident in the eigenvalues computed for Li_2 at $R = 5.051$ a.u. (Table VIII). Again, the discrepancy is at this point of uncertain significance.

TABLE I. Parameters for the neon atom.

A. Basis set (B) and dealiasing (D) functions for the neon atom

Function	Exponent	Orbital type
B	9.485	$1s$
B	15.566	$1s$
B	1.962	$2s$
B	2.864	$2s$
B	4.825	$2s$
B	7.792	$2s$
D	20.0	$1s$
D	15.0	$2s$
D	20.0	$3s$
D	2.86	$3s$
D	5.0	$4s$
D	10.0	$5s$
B	1.452	$2p$
B	2.382	$2p$
B	4.485	$2p$
B	9.135	$2p$
B	10.0	$2p$
B	30.0	$2p$
D	10.0	$3p$
D	20.0	$3p$
D	5.0	$4p$
D	10.0	$4p$
D	5.0	$5p$
D	10.0	$5p$

B. Physical space grid for the neon atom

Grid point	r(a.u.)
1	0.02
2	0.075
3	0.1
4	0.2
5	0.4
6	0.7
7	1.0
8	1.4
9	1.8
10	2.2
11	2.6
12	3.0

TABLE III. Parameters for the H_2 molecule.

A. Basis set (B) and dealiasing (D) functions for the H_2 molecule

Function	Exponent	Orbital type
B	1.16	$1s$
B	1.84	$1s$
B	1.04	$2s$
B	1.67	$2p$
B	2.51	$3d$
D	1.80	$2s$
D	2.50	$2s$
D	3.0	$2p$
D	3.0	$3p$
D	3.0	$3d$

B. Physical space grid for the H_2 molecule[a]

Point	r(a.u.)	θ(rad)
1	0.3	0.0
2	0.44	1.57
3	0.65	3.14
4	0.95	0.94
5	1.41	1.89
6	2.07	3.14
7	3.06	1.57
8	4.5	2.35
9	2.03	1.37
10	4.51	1.48

[a] Values are given at the equilibrium separation $R_e = 1.39$ a.u. Points 9 and 10 are stationary; the remainder move with the atom as R is varied.

basis set. Table V displays equilibrium positions, force constants, and dissociation energies for the H_2 and Li_2 calculations. The pseudospectral results yield quantitative agreement for all quantities for H_2.

The H_2 calculations are very stable with respect to grid placement and dealiasing exponents. Hence, it was unnecessary here (as in the Ne case) to use the least-squares procedure.

D. Li$_2$ molecule

Twenty-two symmetry adapted Slater basis functions [11($+$) functions, 11($-$) functions] were utilized, primarily taken from Ref. 14. Eight dealiasing functions were employed. The canonical orthogonalization procedure removes one basis function, so a total of 18 functions were used in all. The relevant information is summarized in Table VI.

C. H$_2$ molecule

Five symmetry adapted basis functions were used in this calculation, obtained from Ref. 14. These were complemented by five dealiasing functions; there are thus ten grid points in all. Grid and basis set parameters are summarized in Table III. Note that "bonding" points 9 and 10 do not move as the internuclear separation is varied.

Table IV presents a total energy curve for H_2 as a function of internuclear separation. A comparison is made with results from Ref. 15, which employed a somewhat inferior

TABLE II. Total energy and orbital eigenvalues for the neon atom.

Quantity (in a.u.)	This work	Spectral results[a]
Total energy	$-128.547\ 10$	$-128.547\ 05$
ϵ_1	$-32.771\ 2$	$-32.772\ 5$
ϵ_2	$-1.930\ 5$	$-1.930\ 4$
ϵ_3	$-0.850\ 0$	$-0.850\ 4$

[a] Reference 9.

TABLE IV. Potential energy for H_2 as a function of internuclear separation (a.u.).

Separation (a.u.)	This work	Ref. 15	Ref. 14[a]
1.2	$-1.125\ 02$	$-1.124\ 588$	
1.3	$-1.132\ 06$	$-1.131\ 62$	
1.4	$-1.133\ 68$	$-1.133\ 23$	-1.1336
1.5	$-1.131\ 42$	$-1.130\ 97$	
1.6	$-1.126\ 40$	$-1.125\ 93$	
1.8	$-1.111\ 08$	$-1.110\ 97$	
2.0	$-1.091\ 93$	$-1.091\ 03$	
3.0	$-0.989\ 91$	$-0.988\ 00$	

[a] This result was achieved using the same basis set as the pseudospectral calculations.

TABLE V. Spectroscopic constants for Li_2 and H_2.

Molecule	Quantity	This work	Ref. 15
H_2	ωe (cm^{-1})	4580	4582
H_2	De (eV)	3.64	3.64
H_2	Re (a.u.)	1.39	1.39
Li_2	ωe (cm^{-1})	301	326
Li_2	De (eV)	0.17	0.17
Li_2	Re (a.u.)	5.26	5.26

TABLE VI. Parameters for the Li_2 molecule.

A. Basis set (B) and dealiasing (D) functions for the Li_2 molecule[a]

Function	Exponent	Orbital type
B	2.350	$1s$
B	4.300	$1s$
B	0.665	$2s$
B	3.049	$2s$
B	1.553	$3s$
B	2.700	$3s$
B	3.977	$3s$
B	0.700	$3p$
B	1.500	$3p$
B	2.971	$3p$
B	1.151	$3d$
D	0.700	$1s$
D	5.500	$1s$
D	0.700	$3s$
D	5.000	$3s$
D	0.700	$3p$
D	3.000	$3p$
D	2.000	$4p$
D	1.5	$3d$

B. Physical space grid for the Li_2 molecule[b]

Point	r(a.u.)	θ (rad)	Weight
1	0.20	0.31	1.0
2	0.26	0.94	1.0
3	0.34	3.14	2.0
4	0.45	0.31	1.0
5	0.59	0.94	1.0
6	0.77	3.14	2.0
7	1.0	0.31	1.0
8	1.34	0.94	1.0
9	1.75	3.14	2.0
10	2.3	1.57	1.0
11	2.3	0.63	1.0
12	2.46	1.57	1.0
13	2.63	2.82	1.0
14	2.82	0.94	1.0
15	3.02	1.72	1.0
16	3.23	3.14	1.0
17	3.46	0.94	1.0
18	3.71	1.72	1.0
19	3.98	3.14	1.0
20	4.26	1.26	1.0
21	4.56	1.89	1.0
22	4.88	3.14	1.0
23	5.23	1.26	1.0
24	5.60	1.89	1.0
25	6.0	3.14	1.0
26	4.02	1.46	1.0
27	7.09	1.41	1.0
28	10.06	1.45	1.0

[a] Symmetry adapted functions were employed; identical (+) and (−) sets were utilized.

[b] Values are given at the equilibrium separation R = 5.26 a.u. Points 26–28 are stationary; the remainder move with the atom as R is varied. The least-squares weight of each point is also given.

The increased number of functions renders design of an optimized grid more difficult. In particular, calculations with a variety of 18 point grids consistently displayed small (less than 10^{-3}) eigenvalues in the collocation matrix and produced energy errors of as much as 0.01 hartree. Therefore, the least-squares approach of Sec. II C was implemented. The final grid of 28 points provides great stability with respect to grid fluctuation; even large alterations in grid density and angular dispersion produced variation of ≈ 0.001 hartree. Three or four trial variations of the inner and outer radii of the two exponential grids (points 1–10 are between 0.2 and 2.3, points 11–25 are between 2.3 and 6.0) were sufficient to yield the present results. More points were placed in the internuclear region than on the far side so as to accurately average over variation there.

The grid used here is almost certainly larger than necessary; on the other hand, it was constructed in a most primitive manner. As the purpose of the present paper is to demonstrate the potential utility of the pseudospectral approach for general quantum chemical systems, the present calculation is in some ways more relevant than a calculation employing a highly refined grid would be. Note that the least-squares approach minimizes concerns about movement of overlapping grids (which could cause singularities in a collocation procedure).

The resulting potential energy curve for Li_2 is presented in Table VII, along with several comparison values from Ref. 15. Re, ωe, and De are summarized in Table V. Agreement is better than ± 0.0001 hartree in the equilibrium region. At large separation, the larger (± 0.001) discrepancy indicates that some grid reconfiguration is desirable (e.g., the bonding points should perhaps be moved away from the center).

The Li_2 molecule represents a more difficult test for the pseudospectral method than the previous two cases. For a diatomic molecule with three occupied orbitals, complete convergence of the basis set is more problematic. Furthermore, the Li bond is very weak; to obtain accurate estimates of the force constant and bonding strength requires an order of magnitude greater precision than in previous cases.

The results presented in Table V are quite satisfactory. The equilibrium bond length and dissociation energy agree quantitatively, while the vibrational frequency is about 10% lower than the results of Ref. 15. This might be due to the use of a slightly different basis set, or to disagreement at the 0.0001 hartree level between the pseudospectral and spectral calculations. Further investigation will be required to distinguish these alternatives.

It is clear that the pseudospectral calculation reported here could be improved in several ways: increasing the number of functions (both basis set and dealiasing), grid optimization, or optimization of the dealiasing functions. The results presented above demonstrate that even an unoptimized calculation produces acceptable answers. Subsequent publications will describe the effect of employing systematic optimization procedures.

IV. CONCLUSION

This study indicates that the possibility of using pseudospectral methods to substantially accelerate self-consistent

TABLE VII. Potential energy for Li_2 as a function of internuclear separation (a.u.).

Separation (a.u.)	This work	Ref. 15
4.65	− 14.868 91	
4.75	− 14.869 92	
4.77		− 14.869 72
4.85	− 14.870 66	
4.95	− 14.871 20	
5.05	− 14.871 55	
5.07		− 14.871 59
5.15	− 14.871 75	
5.25	− 14.871 82	
5.35	− 14.871 77	
5.37		− 14.871 80
5.45	− 14.871 63	
5.5		− 14.871 48
5.55	− 14.871 41	
5.65	− 14.871 12	
5.75	− 14.870 77	
5.85	− 14.870 37	
5.95	− 14.869 95	
6.00		− 14.868 65
6.05	− 14.869 4	

electronic structure calculations for large molecules is worth pursuing. Of course, explicit tests on large systems will be required to demonstrate this definitively. Work in this direction is currently in progress.

A large number of potential improvements and pathways for exploration are suggested by our results. It will undoubtedly be several years at a minimum before the numerical technology involved in pseudospectral electronic structure calculations is sufficiently mature so that the best choices for basis sets, grid optimization procedures, dealiasing, etc., are established. For example, the present calculations were carried out using Slater basis sets; either numerical basis functions or Gaussian functions might prove to be ultimately superior. Or, perhaps, molecular fragment methods to generate group basis functions would be useful for very large systems. When one considers the amount of numerical work that has been put into quantum chemistry and hydrodynamic/engineering pseudospectral solution of partial differential equations, it is clear that the synthesis of these techniques will be a lengthy process.

Other workers have presented numerical methods for solving the Hartree–Fock equations.[11] In general, these methods do not utilize any sort of physical space grid and hence must ultimately compute two-electron integrals spectrally. It is not clear whether any of these procedures can be efficiently generalized to polyatomics or how they would compare in computation time.

TABLE VIII. Total energy and orbital eigenvalues for Li_2 at $R = 5.051$ (a.u.).

Quantity	This work	Ref. 14
Total energy	− 14.871 55	− 14.8715
ϵ_1^+	− 2.452	− 2.452
ϵ_2^+	− 0.184	− 0.182
ϵ_p^-	− 2.452	− 2.452

A rather different question concerns the calculation of the correlation energy. MCSCF equations are clearly amenable to our approach; the required two-electron integrals can easily be evaluated directly over occupied molecular orbitals, and the approximations made here should be adequate for this purpose. Computation of matrix elements of highly excited virtual orbitals would be less reliable, so that large scale configuration-interaction calculations should be approached with more caution (although use of a larger set of dealiasing functions might facilitate this).

An alternate approach is introduction of a density functional to represent the correlation energy. The numerical technology developed here opens the possibility of solving equations incorporating a *nonlocal* density functional (which, e.g., gives the correct answer for the hydrogen atom in a natural manner). This approach is being pursued in our laboratory.

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