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Spline calculations of the photoionization oscillator strengths of H_3^+

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Summary. We apply spline methods to the problem of calculating continuum excitation probabilities of molecular systems under the influence of electromagnetic fields. Numerical results are given for the H_3^+ molecular ion.

Key words: Numerical calculation – Oscillator strength – Molecular ion

1. Introduction

Until quite recently, *ab initio* calculations on molecules have been performed almost exclusively by expanding the molecular orbitals in terms of analytic basis functions. Although very many accurate basis calculations have been reported, the relevant expansions are often quite lengthy and completeness questions still lend a certain amount of uncertainty to the calculations. From the recent extensive calculation on the H_2O molecule by Feller, Boyle, and Davidson [1], for instance, it is not possible to determine to what extent the discrepancies in the momentum density at low momentum, which they found, were due to basis set error or to other factors in the calculation. A finite basis set, which is determined by minimizing the energy, need not give a reliable description of other properties such as the hyperfine interaction that are especially sensitive to the appearance of orbitals that have a particular spatial form. Numerical calculations, where they are available, provide useful points of reference since they do not depend upon any assumptions about the form of the orbitals and are especially well suited to the study of systems (e.g. anions) and properties that are sensitive to the basis set.

The first numerical self-consistent field calculations for diatomic molecules were carried out by McCullough [2]. For this purpose, the one-electron wave functions were written in the form:

$$\psi_{nm}(\xi, \eta, \phi) = e^{im\phi} \sum_{l} P_l^m(\eta) f_{nlm}(\xi), \tag{1}$$

where ξ, η, ϕ are elliptical coordinates. The expansion in l generally converges uniformly and so accurate results can be obtained in this way. This approach has been extended by McCullough and his co-workers to solve the multiconfiguration Hartree–Fock (MCHF) equations for diatomic molecules and a number of test results have been reported [3]. More recently, McCullough's numerical techniques have been used in conjunction with other theoretical approaches. McCullough, Morrison, and Richman [4] have reported numerical perturbation calculations of the second-order contribution to the correlation energy of several diatomic molecules. Adamowicz and Bartlett [5] have used numerical orbitals generated by McCullough's MCHF code to carry out coupled cluster calculations.

Another numerical approach to diatomic molecules, which, in a sense, is more uncompromising, has been developed by Laaksonen, Pyykko, and Sundholm [6]. In their method, the wave functions are written in the form:

$$\psi_{nm}(\xi, \eta, \phi) = e^{im\phi} f_{nm}(\xi, \eta). \tag{2}$$

When this function is substituted into the Hartree–Fock equations, one obtains two variable partial differential equations for the functions $f_{nm}(\xi, \eta)$ which are then solved numerically. Both this approach and the numerical approach developed previously by McCullough and his co-workers can be applied only to diatomic molecules.

The only numerical calculations on triatomic molecules that we are aware of are those initiated by Alexander, Monkhorst, and their collaborators [7, 8]. They avoid the need of imposing the proper asymptotic dependence of the wave functions simultaneously at the three nuclei by solving the Hartree–Fock equations in momentum space. Only a single singularity then appears at infinity and numerical results can be obtained by using fast Fourier transform techniques with a reasonable amount of time on a supercomputer.

The purpose of this paper is to present the results of a molecular calculation which uses the basis spline and collocation methods. Spline techniques have been used in nuclear and atomic physics for a number of years. Bottcher and Strayer [9] have used spline methods to study the response of a many-fermion system to a dynamical field defined on a lattice. Fischer and her co-workers [10] have used the spline Galerkin method to study correlation effects involving continuum electrons. Johnson, Sapirstein, and their co-workers [11] have used B-splines extensively in perturbation theory calculations. More recent literature contains both systematic expositions of the theory [12, 13] and new applications [14]. Spline methods have the considerable advantage over most other methods that they enable one to treat bound and continuum functions together on the same footing.

2. Basis splines and collocation methods

Given a set of points x_k called knots, a spline of order N, $S^N(x)$, is a piecewise polynomial that satisfies certain continuity conditions. We shall take the knots to be distinct and ordered, $x_k < x_{k+1}$. Between each pair of knots, the spline is a polynomial of degree $N-1$ (the order refers to the number of coefficients); at each knot, the function and derivatives up to the $(N-2)$th are continuous.

The basis (B) splines of order N are a set of functions, $B_k^N(x)$, that form a basis in the space of splines associated with this particular choice of knots. Thus any spline $S^N(x)$ can be represented in terms of them as:

$$S^N(x) = \sum_k \alpha_k B_k^N(x). \tag{3}$$

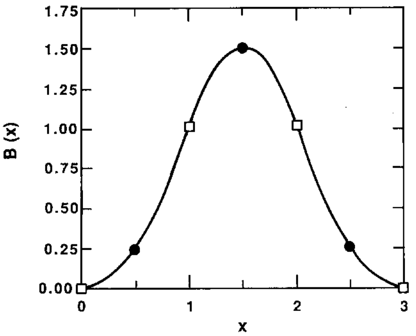

Fig. 1. Basis spline of order $N = 3$. The knots are denoted by open squares, and the collocation points by filled circles

The $B_k^N(x)$ are defined generally by requiring that they be zero outside the range of $N + 1$ consecutive knots $x_k, x_{k+1}, \ldots, x_{k+N}$, and that they satisfy certain boundary conditions. Such a function of order $N = 3$ is illustrated in Fig. 1. Several algorithms are available to construct basis splines from the continuity conditions at the knots and the boundary conditions at the end points [9, 13, 15, 16].

The usefulness of splines for interpolating functions is well known. The function $\psi(x)$ is represented by the interpolent $\hat{\psi}(x)$, where:

$$\hat{\psi}(x) = \sum_{k=1}^{N} \psi^k B_k(x). \tag{4}$$

Here the coefficients are determined by requiring $\hat{\psi}(x) = \psi(x)$ at a set of N data or collocation points, ξ_α, i.e.:

$$\psi(\xi_\alpha) = \sum_{k=1}^{N} B_k(\xi_\alpha)\psi^k. \tag{5}$$

If we define:

$$\psi_\alpha = \psi(\xi_\alpha) \tag{6}$$

$$B_{\alpha k} = B_k(\xi_\alpha) \tag{7}$$

and denote the elements of the inverse of $[B]$ as $B^{k\alpha}$, then the inverse of Eq. (5) is:

$$\psi^k = \sum_{\alpha=1}^{N} B^{k\alpha}\psi_\alpha. \tag{8}$$

This last equation expresses the coefficients that appear in the spline representation, ψ^k, in terms of values of the function at the collocation points.

The collocation method for solving an operator equation:

$$L[\psi] = 0, \tag{9}$$

is intimately related to this interpolation procedure. We obtain N equations for the unknowns ψ^k by requiring that:

$$L\left[\sum_{k=1}^{N} \psi^k B_k\right] = 0 \quad \text{at } x = \xi_\alpha. \tag{10}$$

For linear operators L, this becomes:

$$\sum_{k=1}^{N} \psi^k L[B_k]_{x=\xi_\alpha} = 0. \tag{11}$$

We may now make use of Eq. (8) to eliminate the coefficients ψ^k, and obtain an equation that depends only upon the values of the solution at the collocation points, ψ_α. We obtain:

$$\sum_{\alpha=1}^{N} L_\beta^\alpha \psi_\alpha = 0 \tag{12}$$

where

$$L_\beta^\alpha = \sum_{k=1}^{N} B^{k\alpha} L[B_k]_{x=\xi_\beta}. \tag{13}$$

As a simple example, consider the Schrödinger equation in one dimension:

$$(T+V)\psi = \left[-\frac{1}{2}\frac{d^2}{dx^2} + V(x) \right] \psi = \varepsilon\psi. \tag{14}$$

Equation (13) leads to the following expression for the kinetic energy matrix:

$$T_\alpha^\beta = \sum_{k=1}^{N} B^{k\beta} \left[-\frac{1}{2}\frac{d^2 B_k}{dx^2} \right]_{x=\xi_\alpha}. \tag{15}$$

Furthermore, if V is a local potential, it is represented by a diagonal matrix with elements $V_\alpha = V(\xi_\alpha)$. Under these circumstances the Schrödinger equation assumes the following simple form:

$$\sum_{\beta=1}^{N} (T_\alpha^\beta + V_\alpha \delta_\alpha^\beta)\psi_\beta = E\psi_\alpha. \tag{16}$$

This procedure can be generalized to three dimensions by expanding the wave function in terms of products of basis splines:

$$\psi(x, y, z) = \sum_{ijk} \psi^{ijk} B_i(x) B_j(y) B_k(z). \tag{17}$$

The kinetic energy operator can then be separated into its three Cartesian components, and each of these parts evaluated using Eq. (15).

3. Discussion of Hartree–Fock results

In the independent-particle model, the two electrons of the H_3^+ molecule are described by the same spatial orbital while their spins are in opposite directions. Consequently, the two electrons do not interact by means of the exchange interaction and classical physics provides a correct description of the Coulomb interactions between them.

In our calculations, the Hartree–Fock equations for the molecule were solved in a manner which is entirely analogous to the procedure that is commonly used for atoms [17]. An initial estimate was made of the wave function and this was used to calculate the electron charge density. Poisson's equation was then solved in the space around the three nuclei to obtain the potential energy of the charge distribution. This potential energy term was then substituted into the Hartree–Fock equations for the molecule and the resulting

Table 1. Hartree–Fock results

Number of collocation points	ε_{orb}	E_{tot}
22	−1.19253	1.2436
34	−1.20114	−1.2684
48	−1.20357	−1.2803
64	−1.21080	−1.2929
Alexander, Coldwell, and Monkhorst [8]	−1.21192	−1.30041
Basis set	−1.21166 [20]	−1.30032 [19]

matrix equation was solved using the successive over-relaxation method. This process was continued until self-consistency was achieved. The relevant numerical techniques have previously been used to describe ion-atom scattering processes [18].

Our Hartree–Fock results for different numbers of collocation points are compared with the numerical calculation of Alexander, Coldwell and Monkhorst [8] and the basis set calculations of King and Morokuma [19] and Schwartz and Schaad [20] in Table 1. The energies are given in atomic units which will be used throughout this paper. In this first set of calculations, we did not cluster the collocation points near the nuclear singularities but rather used grids with equally spaced points. For this reason, our results indicate the level of accuracy that one should expect with our methods for an extended cluster of atoms rather than the most precise results that can be obtained for this particular triatomic molecule. The orbital energy which we obtained with 68 collocation points is within a milliHartree of the basis set value. The total energy for the molecule was calculated using the formula:

$$E = 2\varepsilon - \langle J_0 \rangle \tag{18}$$

where ε refers to the orbital energy and J_0 is the (direct) electron-electron interaction potential. Thus our results for the total energy give some indication of the accuracy of our Poisson solver.

4. Calculation of oscillator strengths

4.1. *Summary of the general theory*

The electric dipole contribution to the oscillator strength (f-value) of the molecule for an excitation from the ground state, ϕ_0, to continuum states in the energy range between ε and $\varepsilon + d\varepsilon$ is given by the expression [21]:

$$\left(\frac{df}{d\varepsilon}\right) d\varepsilon = \tfrac{2}{3}(I+\varepsilon)\,|\langle \phi_0 | D | \phi_\varepsilon \rangle|^2 \, d\varepsilon, \tag{19}$$

where I is the ionization energy of the molecule and D is a particular component of the displacement vector, $\hat{r}$. The oscillator strengths satisfy the sum rule:

$$\sum_n \frac{f_n}{\omega_n} + \int_0^\infty \frac{(df/d\varepsilon)\, d\varepsilon}{(I+\varepsilon)} = \tfrac{2}{3}\langle \phi_0 | D^2 | \phi_0 \rangle \tag{20}$$

where the sum is over the bound states and the integration is over the continuum. This is referred to in the literature as the $S(-1)$ sum rule.

In this paper, we shall give the contributions to the $S(-1)$ sum rule rather than the oscillator strengths themselves. Our reasons for this are twofold. First, since the individual contributions to the left-hand side of Eq. (20) must all add up to give the right-hand side of that equation, calculating the contributions to the sum rule leads to an immediate, preliminary check of the results of this first calculation. Second, by comparing our results with the integrated value, we gain direct information of the importance of excitations to other bound states. These excitations are important in their own right since they provide pathways for the molecular dissociation.

According to Eqs. (19) and (20), the contribution to the sum rule from excitations to the continuum may be written:

$$C(-1) = \tfrac{2}{3}\int_0^\infty d\varepsilon \langle \phi_0 | D | \phi_\varepsilon \rangle \langle \phi_\varepsilon | D | \phi_0 \rangle. \tag{21}$$

For reasons that will become apparent shortly, we now insert into this expression for $C(-1)$ the operator:

$$\delta_\Delta(H-E) = \frac{1}{\sqrt{\pi}\Delta} e^{-(H-E)^2/\Delta^2}, \tag{22}$$

where Δ is a small positive number. In this way, we obtain the following expression:

$$C(-1)_E = \tfrac{2}{3}\int_0^\infty d\varepsilon \langle \phi_0 | D \left[\frac{1}{\sqrt{\pi}\Delta} e^{-(H-E)^2/\Delta^2} \right] | \phi_\varepsilon \rangle \langle \phi_\varepsilon | D | \phi_0 \rangle. \tag{23}$$

When it operates on the state, $|\phi_\varepsilon\rangle$, the operator, $\delta_\Delta(H-E)$ will clearly produce the kind of sharply peaked function which is used in a representation of the Dirac delta function. Thus, for small values of Δ, the effect of inserting this operator into Eq. (21) will be to extract from the sum rule the contribution from Coulomb waves having an energy near E. We also note that if Δ is sufficiently small, the overlap of the resultant Gaussian functon with the bound states can be neglected, and the set of states $|\phi_\varepsilon\rangle\langle\phi_\varepsilon|$ can be regarded as a complete set. Taking advantage of this fact, Eq. (23) can be written:

$$C(-1)_E = \tfrac{2}{3}\langle \phi_0 | D \frac{1}{\sqrt{\pi}\Delta} e^{-(H-E)^2/\Delta^2} D | \phi_0 \rangle. \tag{24}$$

Methods that can be used to take into account and remove the contribution of the bound states have been given previously [14].

Equation (24) can be further simplified by introducing an operator which is the square root of $\delta_\Delta(H-E)$. We define the operator, $F(E)$, which we shall refer to as a Gaussian filter, by the equation:

$$F(E) = \left[\frac{1}{\sqrt{\pi}\Delta} \right]^{1/2} e^{-(H-E)^2/2\Delta^2}. \tag{25}$$

Making use of this definition, Eq. (25) can be written:

$$C(-1)_E = \tfrac{2}{3}\langle \phi_0 | D F(E) F(E) D | \phi_0 \rangle. \tag{26}$$

Finally, Eq. (26) can be written as a constant times an inner product by introducing the following state vector:

$$|\chi\rangle = F(E)D|\phi_0\rangle. \tag{27}$$

Since the operators $F(E)$ and D are self-adjoint, the contribution to the sum rule becomes simply:

$$C(-1)_E = \tfrac{2}{3}\langle\chi|\chi\rangle. \tag{28}$$

The state, $D|\phi_0\rangle$, which appears in Eq. (27), corresponds to a wave packet of excited states. The Gaussian filter, $F(E)$, projects out of the wave packet the contribution that is due to the Coulomb waves in a particular energy range.

4.2. The damped relaxation method for obtaining operator products

In the preceding section, it was found that the contributions to the sum rule may be evaluated by operating upon $D|\phi_0\rangle$ with the exponential operator, $F(E)$. This may be accomplished by expanding $F(E)$ in a power series. We shall now describe a more effective, iterative method for evaluating the product of an exponential operator and a wave function.

Using L'Hôpital's rule and elementary properties of the exponential function, one may readily derive the following representation of the exponential:

$$e^{-\alpha} = \lim_{M\to\infty}\left[1 - \frac{\alpha}{M}\right]^{-M}. \tag{29}$$

In our case, α has the value:

$$\alpha = \frac{(H-E)^2}{2\Delta^2}. \tag{30}$$

We would like now to make use of the representation of the exponential function of Eq. (29) to evaluate products of the form $e^{-\alpha}\psi$. For a given value of M, we define:

$$\Omega = 1 + \frac{\alpha}{M}. \tag{31}$$

With this notation, $(1/\Omega)^M\psi$ defines a representation of the operator product that we wish to evaluate. We would like to define an iterative scheme for generating this representation from lower powers of $1/\Omega$. In order to do this, we define:

$$\psi_N = \Omega^{-N}\psi, \qquad 1 \leqslant N \leqslant M. \tag{32}$$

This equation may be used to show that:

$$\Omega\psi_N = \Omega^{-(N-1)}\psi, \tag{33}$$

or

$$\Omega\psi_N = \psi_{N-1}. \tag{34}$$

We may thus solve Eq. (34) to generate the function, ψ_N, from the function, ψ_{N-1}, which we suppose to be known. This procedure may be used successively to generate the function, ψ_M, which according to Eqs. (29), (31), and (32), forms a representation of $e^{-\alpha}\psi$. In order to solve Eq. (34), we define the iterative scheme:

$$\psi_N^{(i+1)} = \psi_N^{(i)} + \tau \left[1 + \frac{T}{\mu^2}\right]^{-1} \{\Omega\psi_N^{(i)} - \psi_{N-1}\}. \tag{35}$$

This iterative procedure for generating a representation of the exponential function is analogous to the successive over-relaxation method of matrix algebra. It is very easy to verify since for each iteration one constructs the residual of the equation. Without delay, we shall thus describe some of the checks which we have made of the exponential representation itself.

Consider the convolution integral:

$$\tilde{P}(E) = \int_0^\infty [\delta_\Delta(\varepsilon - E)]_M P(\varepsilon)\, d\varepsilon, \tag{36}$$

where $P(\varepsilon)$ is the normalized function:

$$P(\varepsilon) = N_p \sqrt{2\varepsilon}\, e^{-2\varepsilon} \tag{37}$$

and where:

$$[\delta_\Delta(\varepsilon - E)]_M = \frac{1}{\sqrt{\pi}\Delta} \left[1 - \frac{(\varepsilon - E)^2}{\Delta^2 M}\right]^{-M}. \tag{38}$$

The function, $[\delta_\Delta(\varepsilon - E)]_M$, is the representation of the function, $\delta_\Delta(\varepsilon - E)$, which one gets by using the M-th term on the right-hand side of Eq. (29) to represent the exponential function. To the extent that this function equals the delta function, $\delta(\varepsilon - E)$, the integral in Eq. (36) will reduce to $P(E)$, and $\tilde{P}(E)$ will equal $P(E)$. The functions, $P(E)$ and $\tilde{P}(E)$, are compared in Figs. 2–4 for different values of M and Δ. In each case, $P(E)$ corresponds to the solid line in the figure while $\tilde{P}(E)$ corresponds to the lower of the two broken lines. We see

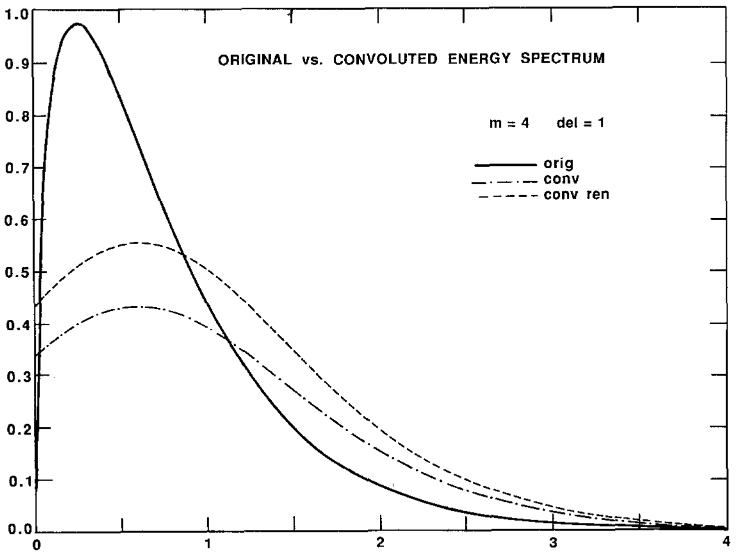

Fig. 2. Original function, $P(r)$, plotted together with convolution integral $\tilde{P}(r)$ and a renormalized convolution integral. For this figure $M = 4$ and $\Delta = 1.0$

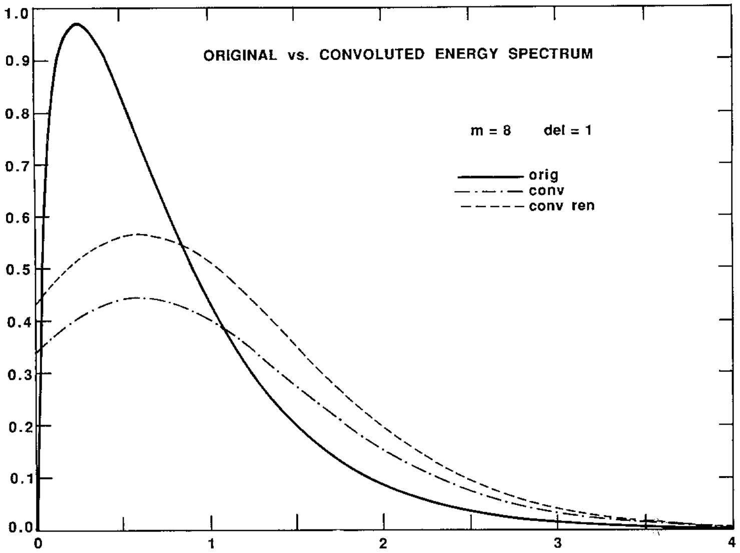

Fig. 3. Original function, $P(r)$, plotted together with convolution integral $\tilde{P}(r)$ and a renormalized convolution integral. For this figure $M = 8$ and $\Delta = 1.0$

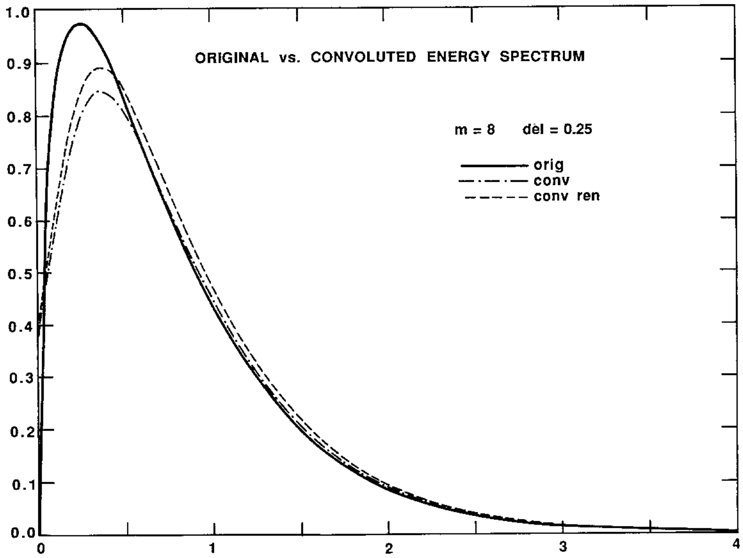

Fig. 4. Original function, $P(r)$, plotted together with convolution integral $\tilde{P}(r)$ and a renormalized convolution integral. For this figure $M = 8$ and $\Delta = 0.25$

that increasing M from four to eight for a given value of Δ does not significantly change the accuracy of the representation; however, changing the value of Δ from 1.0 to 0.25 does have an important effect.

We also checked our projection procedure by using it to calculate the Fourier transform of a known (Gaussian) function. This was done by replacing the full Coulomb Hamiltonian (H) in Eq. (23) with the free electron kinetic energy

Table 2. Contributions to sum rule

E	$C(-1)_E$
1.0	2.33×10^{-3}
2.0	7.31×10^{-6}
3.0	8.36×10^{-7}
4.0	1.29×10^{-6}
5.0	3.98×10^{-7}

Integrated value = 0.5313

operator. The Fourier transform, which we obtained in this way, was compared with the value we obtained by analytically carrying out the integration. The use of a Gaussian trial function provides a stringent check of the projection procedure since it is such a sharply peaked function. By comparing our result with the analytic value, we were able to check our numerical methods over a wide range of energies.

4.3. *Results and discussion*

The contributions to the oscillator strength sum rule, which are due to excitations to the continuum, are given in Table 2. All energies are in atomic units. At the bottom of the table, we have also given the integrated value, which includes the effect of excitations to both bound and free members of the series. As can be seen from the table, the contributions decline dramatically as the energy increases from 1.0 to 3.0. By comparing the contributions of excitations to the continuum with the integrated value, it is also clear that the largest effect is due to excitations to the bound members of the series. As we have indicated previously, these excitations are important in their own right since they provide pathways for molecular dissociation.

In future work, we intend to study the excitations to the bound states. For the bound excited states of light triatomic molecules, the single configuration Hartree–Fock method often fails and a multi-reference formalism of the kind we have previously developed for atoms [22] is very appropriate. In our future work, we would also like to use grids that cluster the collocation points near the nuclear singularities. For light molecules, this is possible to a large extent even with the one-dimensional spline formalism that we have used in this calculation. Spline calculations for large molecular systems with an accuracy beyond the milliHartree level may have to await the development of three-dimensional spline algorithms.

In concluding, we would also like to indicate briefly how these numerical techniques could be applied to the coupled cluster theory. One general way of approching the coupled cluster formalism is through many-body perturbation theory [23]. The single-particle excitations that arise in this way can easily be included using the same numerical methods that we have used in this paper for the Hartree–Fock method. The two-particle effects have already been reported for atoms [11]. A straight forward extension of these methods to molecules would be quite time consuming although calculations of this kind are surely possible on modern concurrent machines such as the hypercube at the Oak Ridge National Laboratory. At the present time, it would probably be preferable to include pair effects within the framework of some approximation scheme such as the pair natural orbital approach [23, 24, 4].

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