Numerical Solution of the \((1s1s)\) and \((1s2s)\) Hydrogenic Pair Equations

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The pair functions which determine the exact first-order wave function for the ground state of the three-electron atom have been found with the matrix finite-difference method. The second- and third-order energies for the \((1s1s)\) \(1S\), \((1s2s)\) \(3S\), and \((1s2s)\) \(1S\) states of the two-electron atom are presented along with contour and perspective plots of the pair functions.

I. INTRODUCTION

It was previously shown that the functional coefficients of the partial-wave expansion for the first-order pair functions could be obtained with the matrix finite-difference (MFD) method. Taking the full electron interaction as the perturbation, the method has been extended to the three pair equations that determine the first-order wave function for the lithium isoelectronic series. The pair functions are independent of the nuclear charge and can be used to construct the first-order wave functions for other atoms when the remaining hydrogenic pair functions are determined. The method is not variational and therefore can be applied without orthogonality constraints to the excited pair functions that are not the lowest of their symmetry. In addition, the calculation of the total second- and third-order energy involves none of the difficult integrals that occur for the complicated variational functions containing interelectronic coordinates.

The solution of the two-electron equations is described in Sec. II. The second- and third-order pair energies are compared to accurate variational results in Sec. III. Finally, the contour and perspective plots are presented for each of the pair functions.

II. SOLUTION OF FIRST-ORDER PAIR EQUATION

Since the pair functions are spherically symmetric, the partial-wave expansion for each is simply

\[
U(r_1, r_2) = \sum_l u_l(r_1, r_2) P_l(\cos \theta_{12}).
\]  

By substituting this into the pair equation, multiplying both sides by \(P_l(\cos \theta_{12})\), and integrating over the angular variables, the following partial differential equation for \(u_l(r_1, r_2)\) is obtained:

\[
\begin{align*}
&- \frac{1}{2} \frac{1}{r_1^2} \frac{\partial}{\partial r_1} \left( r_1^2 \frac{\partial}{\partial r_1} \right) u_l(r_1, r_2) + \frac{1}{2} \frac{\partial}{\partial r_2} \left( r_2^2 \frac{\partial}{\partial r_2} \right) - \frac{1}{r_1} - \frac{1}{r_2} \\
&= \left( E_{\text{pair}} - \frac{l(l+1)}{2r_1^2} - \frac{l(l+1)}{2r_2^2} - \epsilon_1 - \epsilon_2 \right) u_l(r_1, r_2),
\end{align*}
\]  

where \(E_1 = \frac{\delta}{4} \) for the \((1s1s)\) pair, \(E_1 = \frac{\mu}{2} \) for the \((1s2s)\) \(3S\) pair, and \(E_1 = \frac{\mu}{4} \) for the \((1s2s)\) \(1S\) pair. The function \(R\) is the radial part of the zero-order function for each state. The boundary conditions on \(u_l(r_1, r_2)\) require that it be finite for \(r_1 = 0\) or \(r_2 = 0\) and that it vanish for \(r_1 = 0\) or \(r_2 = \infty\). The set of equations for the functional coefficients are not coupled and are solved independently for each partial wave using the MFD method.

The details of the numerical analysis have already been discussed; however, two important modifications have been introduced which allow the diffuse excited states to be handled efficiently. First, the radial cutoff [the point at which \(u_l(r_1, r_2)\) is required to vanish] for these states must be taken farther out than for the \((1s1s)\) pair previously treated. Therefore, even with extrapolation, a very large number of points are needed to achieve comparable accuracy. To avoid this difficulty, the following coordinate transformation was introduced into the pair equation:

\[
r_1 = x_1^4, \quad r_2 = x_2^4.
\]

The grid points in the transformed system are closely spaced near the nucleus and farther apart in the tail regions, as viewed in the untransformed system. This means that by using a large radial cutoff and relatively few points, the regions important to the accurate solution of (2) are not neglected.

The second modification in the MFD method was to improve the difference approximation of the derivatives. Instead of truncating the difference expansion at the second difference approximation, the fourth difference is included, giving the following improved approximation for the second derivative:
### TABLE I. Extrapolation of the partial-wave contributions to $E_2$ for the (1s1s)$^1S$ pair.\(^a\)

<table>
<thead>
<tr>
<th></th>
<th>$S$ wave</th>
<th>$P$ wave</th>
<th>$D$ wave</th>
<th>$F$ wave</th>
<th>$G$ wave</th>
<th>$I$ wave</th>
</tr>
</thead>
<tbody>
<tr>
<td>$30$</td>
<td>0.12679967</td>
<td>0.03638709</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$45$</td>
<td>0.12631823</td>
<td>0.02630393</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>$60$</td>
<td>0.12592778</td>
<td>0.02735592</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$75$</td>
<td>0.12572696</td>
<td>0.02703725</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Results were obtained on a linear grid with a 12-a. u. cutoff using second differences only.

### TABLE II. Extrapolation of the partial-wave contributions to $E_2$ for the (1s2s)$^3S$ pair.\(^a\)

<table>
<thead>
<tr>
<th></th>
<th>$S$ wave</th>
<th>$P$ wave</th>
<th>$D$ wave</th>
<th>$F$ wave</th>
<th>$G$ wave</th>
<th>$I$ wave</th>
</tr>
</thead>
<tbody>
<tr>
<td>$30$</td>
<td>0.00498619</td>
<td>0.00160636</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>$45$</td>
<td>0.00435858</td>
<td>0.00130472</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>$60$</td>
<td>0.00415249</td>
<td>0.00120160</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$75$</td>
<td>0.00406071</td>
<td>0.00115524</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Results for the $S$ wave were obtained on a linear grid with a 24-a. u. cutoff. Remaining waves were obtained with a 20-a. u. cutoff. Both calculations used second differences only.
NUMERICAL SOLUTION OF \( (1s1s) \) AND \( (1s2s) \)...
where $D$ is a banded matrix. The second-difference approximation produces a symmetric matrix, as does the fourth-difference approximation with the modified boundary conditions. However, the mixed-difference method leads to an unsymmetric matrix. The difference equations were solved with Gaussian elimination for the $l = 0$ partial wave and with the Gauss-Seidel method for $l > 0$. It was found that for the higher partial-wave equations, the Gauss-Seidel method converged extremely fast, while for the $S$ wave, the method diverged. Because the Gaussian elimination method is more efficient for symmetric matrices, the mixed-difference approximation was not used for the $S$ wave, but was used for each of the higher waves.

III. CALCULATION OF SECOND- AND THIRD-ORDER ENERGIES FOR TWO-ELECTRON STATES

The partial-wave equations for each pair function were solved using both the usual second-difference approximation and the improved difference formula given by (19). The second-order energy for each pair was found from

$$E_2(\text{pair}) = \sum_{l=0}^{N} \frac{1}{2l+1} \int u_l(r_1, r_2) \left( \frac{r_1^2}{r_2^2} \right) - E_1(\text{pair}) \times R(r_1, r_2) r_1^2 r_2^2 dr_1 dr_2. \quad (6)$$

The radial integral was calculated by the trapezoidal rule. The calculations were carried out at several grid sizes, and the results were extrapolated with Richardson's method. Therefore, the difference and quadrature errors were eliminated in one step. Note that the perturbation energies are defined according to $E = \sum E_n Z^{-n}$. The extrapolation tables for the partial-wave contributions to $E_2$ for the $(1s1s)$ pair are given in Table I. The results were found using the second-difference approximation and the untransformed (linear) grid with a 12-a.u. cutoff. The first column of each table lists the number of strips used in each direction. The second column gives the initial results, and the remaining columns contain the extrapolants. The latter were obtained using different sets of results from the first column. By displaying the results in this

<table>
<thead>
<tr>
<th>$N$</th>
<th>20</th>
<th>25</th>
<th>30</th>
<th>35</th>
<th>40</th>
<th>Extrapolant</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_2(6)$</td>
<td>-0.139 424 67</td>
<td>-0.125 105 29</td>
<td>-0.118 632 54</td>
<td>-0.115 101 83</td>
<td>-0.112 948 19</td>
<td>-0.106 621 65</td>
</tr>
<tr>
<td>$E_2(1)$</td>
<td>-0.007 345 60</td>
<td>-0.007 008 53</td>
<td>-0.006 840 46</td>
<td>-0.006 744 12</td>
<td>-0.006 683 65</td>
<td>-0.006 497 85</td>
</tr>
<tr>
<td>$E_2(2)$</td>
<td>-0.001 256 44</td>
<td>-0.001 128 58</td>
<td>-0.001 062 79</td>
<td>-0.001 024 85</td>
<td>-0.001 001 08</td>
<td>-0.000 929 29</td>
</tr>
<tr>
<td>$E_2(3)$</td>
<td>-0.000 425 50</td>
<td>-0.000 306 80</td>
<td>-0.000 262 10</td>
<td>-0.000 209 63</td>
<td>-0.000 292 69</td>
<td>-0.000 253 55</td>
</tr>
<tr>
<td>$E_2(4)$</td>
<td>-0.000 197 94</td>
<td>-0.000 101 80</td>
<td>-0.000 040 39</td>
<td>-0.000 127 84</td>
<td>-0.000 098 77</td>
<td>-0.000 094 75</td>
</tr>
<tr>
<td>$E_2(5)$</td>
<td>-0.000 095 76</td>
<td>-0.000 027 06</td>
<td>-0.000 073 81</td>
<td>-0.000 068 56</td>
<td>-0.000 061 15</td>
<td>-0.000 042 67</td>
</tr>
<tr>
<td>$E_2(6)$</td>
<td>-0.000 067 84</td>
<td>-0.000 033 61</td>
<td>-0.000 044 11</td>
<td>-0.000 038 42</td>
<td>-0.000 034 62</td>
<td>-0.000 021 78</td>
</tr>
<tr>
<td>$E_2(7)$</td>
<td>-0.000 045 12</td>
<td>-0.000 023 94</td>
<td>-0.000 028 74</td>
<td>-0.000 024 68</td>
<td>-0.000 021 92</td>
<td>-0.000 012 19</td>
</tr>
<tr>
<td>$E_2(8)$</td>
<td>-0.000 031 63</td>
<td>-0.000 024 42</td>
<td>-0.000 019 92</td>
<td>-0.000 016 93</td>
<td>-0.000 014 87</td>
<td>-0.000 017 34</td>
</tr>
<tr>
<td>$E_2(9)$</td>
<td>-0.000 023 07</td>
<td>-0.000 017 79</td>
<td>-0.000 014 44</td>
<td>-0.000 012 19</td>
<td>-0.000 010 62</td>
<td>-0.000 004 69</td>
</tr>
<tr>
<td>$\sum E_2$</td>
<td>-0.148 925 58</td>
<td>-0.133 981 62</td>
<td>-0.127 183 31</td>
<td>-0.123 462 06</td>
<td>-0.121 187 56</td>
<td>-0.114 485 74</td>
</tr>
<tr>
<td>$E_3$</td>
<td>-0.000 715 79</td>
<td>-0.002 951 08</td>
<td>-0.003 667 29</td>
<td>-0.003 993 78</td>
<td>-0.004 173 63</td>
<td>-0.004 625 79</td>
</tr>
</tbody>
</table>

TABLE VI. Extrapolated results for the $(1s2s) 1S$ pair on the square-root grid.
manner, it is possible to determine whether the extrapolants are converging from above or below the true value. The partial-wave contributions from all but the $S$ wave are converging from below and have converged to at least six decimal places. The results for the $S$ wave appear to oscillate, but the suitable produced by the 45-, 60-, and 75-
strip calculations is converging smoothly from below. The extrapolation tables for the $S$ and $S_{1/2}$ excited states are given in Tables II and III. These results illustrate the need for the modifications that were discussed in Sec. II. The 120-

wave calculation required the solution of nearly 14,000 linear equations which took about 1 h on the IBM 360-75. The $S$-wave cutoff was taken at 24 a. u., which was still not far enough from the nucleus. Clearly, it was not practical to re-solve the equations with a larger cutoff. The functions for $l > 0$ were much less diffuse and could be obtained easily in only a few minutes. For the $S$ state, these waves were nearly converged without extrapolation. The $S$ wave for both states converged from above.

The three-pair equations were re-solved using the fourth-difference approximation and the transformed (square root) grid. The initial results and the final extrapolants for the first 10 partial-wave contributions to $E_4$ are given for the three states in Tables IV-VI. In addition, the third-order and total energies are also given for $Z = 2$. The radial cutoff was taken at 32 a. u. for all three calculations. The first important result that should be noted is that relatively few points were needed to obtain better accuracy than the linear-grid calculations. All of the numbers were found at one time with the same program, and the total time was about 1 h. This could have been reduced to about 20 min, if fewer grids were used. For example, the results from the 20-, 25-, and 30-strip calculations gave the following extrapolants for the (1s1s) pair:

\[ E_4(0) = -0.12532 \text{ a.u.}, \]
\[ E_4(1) = -0.02648 \text{ a.u.}, \]
\[ E_4(2) = -0.00387 \text{ a.u.}, \]
which agree well with the best results.

The third-order energy for each pair was calculated from

$$E_3^{(\text{pair})} = \sum_{\ell, r_1, r_2} \Omega^2 (0, l', 0) \int u_1(r_1 r_2) \frac{r_1^2}{r_2} \, dr_1 \, dr_2$$

$$- \sum_{\ell, r_1, r_2} \Omega^2 (0, l', 0) \int u_1(r_1 r_2) \frac{r_2^2}{r_1} \, dr_1 \, dr_2$$

$$- 2E_2^{(\text{pair})} \int u_0(r_1 r_2)$$

where

$$\Omega^2 (0, l', 0) = \prod_{\ell, r_1, r_2} \frac{1}{2l + 1} \int u_1(r_1 r_2)$$

The total energies were found for the helium atom and compare well to the following values given by Knight and Scherr:

$$E_1^{(1s1s, 1s)} = -2.90331692 \text{ a.u.},$$

$$E_1^{(1s2s, 3s)} = -2.17398777 \text{ a.u.},$$

$$E_1^{(1s2s, 1s)} = -2.14611980 \text{ a.u.}$$
The partial-wave contributions to the second-order energy have been calculated variationally by Byron and Joachain. The contributions found by the two numerical approximations are compared to variational results in Tables VII-IX. For the (1s1s) pair, the first three columns agree closely for each partial wave. The values of $E_2(1)$ and $E_2(2)$ predicted by Knight and Scherr are less accurate, but their total second-order energy was not found by a partial-wave expansion and represents the most accurate value. The total $E_2$ given by
Byron and Joachain contain contributions from partial waves not given in the table. The third-order energy shows somewhat worse agreement which is due in part to the finite number of partial waves used in the calculation. Comparison of the results for the $^3S$ and $^1S$ excited states illustrates the importance of the accurate difference formula and the increased cutoff. The agreement with Knight and Scherr is generally better than for the ground state. In fact, Knight recently reevaluated the $^1S$ second-order energy and found the improved value to be $-0.114509$ a.u. This indicates that the fourth-difference value is the most accurate of those given in Table IX. The variational calculation of the partial-wave contributions by Byron and Joachain compares less favorably for this pair. Since this is not the lowest state of its symmetry, it is expected that the variational method would have more difficulty. However, the main
reason for the disagreement in this case is due to the choice of a configuration-interaction-type trial function for the functional coefficients.

Schwartz¹⁰ gave an asymptotic formula for $E_2(l)$, which Byron and Joachain⁸ used to estimate the contributions from partial waves with $l > 20$ for the ground state and with $l > 6$ for the excited states. They obtain $E_2(l > 10) = -0.000042$ a.u., $E_2(l > 6, S) = -0.000001$ a.u., and $E_2(l > 6, P) = -0.000041$ a.u. If the contribution for the ground state is added to the second-difference result, we obtain $-0.157661$ a.u., which agrees well with the correct value of $-0.157666$ a.u. The fourth-difference results predict that $E_2(l > 6, S) = -0.0000016$ a.u. and $E_2(l > 6, P) = -0.0000069$ a.u., using the accurate values of the second-order energy given by Knight⁹ for comparison. Because the functional coefficients $u_1(r_1r_2)$ are found as arrays of numbers, it is not possible to communicate them in a compact form. Each coefficient could be polynomial fitted, but these results would still require a large amount of space to display. However, qualitative information can be given in the form of contour plots of each pair function. The discussion of the plots of the functional coefficients for the three pairs is given in Sec. IV.

IV. CONTOUR AND PERSPECTIVE PLOTS OF PAIR FUNCTIONS

The numerical functions found on the linear grid were plotted over a square region with the boundaries set at one-half the radial cutoff. In each con-
tour plot, the nucleus is located at the lower left corner, with the \( r_1 \) and \( r_2 \) axes running horizontally and vertically from this point. The positive contours are given by solid lines and the negative contours by dashed lines. Because of an artifact of the Calcomp plotter, some of the solid lines tend to break up in regions of small \( r_1 \) or \( r_2 \). These should not be mistaken for negative contours, which are dashed lines in all regions. Each functional coefficient was multiplied by \( r_1 r_2 \) and plotted with a constant contour interval. The values of the contour interval and of the largest positive and negative contours for the three states are given in Table X. Ideally, these values should have been found for several grids and extrapolated to obtain quantitative results. Instead, the values are given for the particular function plotted and represent the exact results to no more than two or three significant figures.

Figure 1 gives the plots for the first six partial waves of the first-order function for the \( \text{ls}_{1s} \) pair. For \( l=0 \), the effect on the zero-order function is to subtract amplitude in the region close to the nucleus and along the line \( r_1=r_2 \). The functional coefficients for \( l>0 \) are negative in all regions, becoming more peaked along \( r_1=r_2 \) as \( l \) is increased. These waves have a simpler form, since the orthogonality to the zero-order function is ensured by the angular factor. In Fig. 2, the perspective plots of the first two partial waves are given along with the zero-order, first-order, and total functions. The viewer’s orientation for these plots is shown in
Fig. 3. Each perspective plot was drawn to the same scale and can be directly compared. The contour plots of $\psi_0$, $\psi_1$, and $\psi$ for all three pairs are given in Fig. 4. The total first-order function was found by taking $\theta_{12} = 0$ and summing the partial-wave components:

$$\psi_1 = \sum_{l=1}^{L_{\text{max}}} \mu_l(r_1, r_2);$$

then the total function was approximated by

$$\psi = \psi_0 + \psi_1.$$  \hspace{1cm} (9)

The first-order function shows a deep minimum near the nucleus and two well-separated maxima farther out. When this is added to the zero-order function, the total function is found to have two separated maxima with a minimum along $r_1 = r_2$.

This is qualitatively what the exact solution should look like.

The partial-wave contributions to the first-order function for the $^3S$ state are shown in Fig. 5. The trends are approximately the same as for the ground state except that the effects contributed by higher partial waves are smaller. This is expected because of the exact node at $r_1 = r_2$. From the perspective plots of $\psi_0$ and $\psi$ given in Fig. 6, the total first-order function serves to reduce the amplitude near the nucleus and increase it farther out (for the positive region). The contour plots of the functional coefficients for the $^3S$ excited state are shown in Fig. 7. They exhibit the intricate nodal structure expected for a state which is not the lowest of its symmetry. In each case, the functions subtract...
amplitude from the nuclear region and build amplitude in the region $r_1$, $r_2 \approx 4$ a.u., when added to $\psi_0$. In Figs. 4 and 8, the zero-order function is shown to have a maximum at $r_1$, $r_2 \approx 1$ a.u. and separated minima at $(r_1, r_2) \approx (1, 6)$ a.u. and $(r_1, r_2) \approx (6, 1)$ a.u. Adding the first-order function for $\theta_{12} = 0$, the total function has two maxima occurring at $(r_1, r_2) \approx (1, 1.75)$ a.u. and $(r_1, r_2) \approx (1.75, 1)$ a.u. The minima are moved out from 6 to 8 a.u. For both of the excited states, the perspective plots are drawn to the same scale as the ground state, so that amplitudes for the three states can be directly compared.

V. DISCUSSION

The MFD method has been shown to be capable of solving the first-order pair equations for the many-electron atom with accuracy comparable to the best variational results. In addition, because the method is not variational, it is quite easily applied to pairs that are not the first of their symmetry. The same programs that were used here for the $(1s1s)$ and $(1s2s)$ pairs can be applied without modification to any $(1sn$s) pair. Since the results are independent of the nuclear charge, these pair functions can be used in the construction of the first-order wave function for any state of a general many-electron atom. In order to do this, the remaining pair functions, $(nsn's)$, $(npp'n')$, $(nn'n')$, etc., where $n$ may be the same as $n'$, need to be calculated. These results will be reported in a
series of future papers. Once the total first-order wave function has been constructed from the set of pair functions, the total second- and third-order energy of the atom are easily calculated. The same quadrature and extrapolation techniques that are used for the pair energies can be applied, and the difficult integrals that have plagued the variation methods are avoided.

3The first-order solutions for the \(1s2p\) pairs have already been obtained and will be communicated in a future paper.