# Nodal Boundary Condition Method for Atomic Wave Functions and Transition Probabilities*

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A method is presented for computing valence atomic wave functions and transition probabilities. This method, called here the "nodal boundary condition method," is a modified self-consistent-field approach which makes some use of experimental term values in order to eliminate the need for calculating wave functions for the core electrons. As an application, the method is used to compute eigenvalues, wave functions, and oscillator strengths for thirteen atoms and ions having two valence electrons.

## I. INTRODUCTION

THERE is an increasing need for reasonably accurate atomic transition probabilities, or "oscillator strengths," particularly for astrophysical applications. This paper will discuss a method for calculating these quantities. The approach, which is semiempirical, uses experimental atomic energy levels to help in computing self-consistent-field wave functions. These wave functions are then used to calculate the matrix elements involved in the transition.

The method, which we will call the "nodal boundary condition method," is applicable to atoms having two or more valence electrons outside complete inner shells. For many of these atoms, both experimental and theoretical oscillator strength information is very meager. As an application, the method is used to compute some oscillator strengths for thirteen atoms and ions having two electrons outside closed shells.

The remainder of this introduction will discuss two well-known approaches to the problem of calculating wave functions and transition probabilities, the self-consistent-field (SCF) Hartree-Fock method, and the Coulomb approximation Bates-Damgaard method. Section II will introduce the nodal boundary condition method itself. Section III discusses the evidence for stability of the inner nodes of valence radial wave functions, which permits a considerable simplification over the full SCF calculations. Section IV describes the calculation of wave functions and transition probabilities for atoms with two valence electrons, and Sec. V gives the results. General conclusions and possible further applications are discussed in Sec. VI. Finally, some details of the calculations are given in the Appendix.

The problem of obtaining accurate transition probabilities reduces largely to that of computing accurate atomic wave functions. The dipole-moment matrix element, whose square is proportional to the transition probability for allowed transitions, is usually quite sensitive to these wave functions.

The most generally successful approach to the problem of obtaining accurate wave functions is the variational method. One technique is to assume that the wave functions have some particular analytic form containing unknown parameters which can be varied to minimize the energy. This has been applied very successfully to the helium atom, and is now being increasingly used for many-electron atoms. By far the most common way to employ the variational method is the self-consistent-field (SCF) approach, which assumes that the total wave function can be approximately written as a product of one-electron functions. If a simple product is used, one obtains the Hartree equations (without exchange), or if instead an antisymmetric product is used, one obtains the Hartree-Fock equations (with exchange). These are integrodifferential equations which can be solved numerically by iterative methods.[1] In order to find the wave function for one electron, one must calculate the wave functions for all. The calculations are lengthy, but with modern computers approximate variational wave functions can be found by using programs already developed.[2]

A completely different approach has had considerable success in treating atoms having only a single valence electron. In 1949, Bates and Damgaard[3] made transition probability calculations based on two important assumptions. First, they assumed the valence electron moves in a pure Coulomb field corresponding to the nuclear charge minus the charge of all the other electrons. That is, they assumed that the true potential in which a valence electron moves is represented sufficiently accurately by the asymptotic potential at large radii, where it is outside the inner electron shells. Second, they assumed that the energy eigenvalue of the electron is the same as its experimental binding energy or ionization potential. This is equivalent to the assumption that other electrons aren't disturbed when the valence electron is removed from the atom.

These are reasonable approximations for atoms with one valence electron, as long as we are interested only

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[1] D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957).

[2] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).

[3] D. R. Bates and A. Damgaard, Phil. Trans. Roy. Soc. (London) A242, 101 (1949).

in the parts of the radial wave function at fairly large radii, where the potential is nearly Coulomb. Fortunately, the dipole moment matrix element, which contains in the integrand the product of initial and final wave functions and the radius "$r$" of the active electron, has appreciable contributions only at fairly large radii, almost entirely outside the inner electron shells.

Bates-Damgaard transition probabilities often agree very well with experimental values, particularly for the alkali atoms, such as Li I, Na I, and K I. In fact, this simple Coulomb-approximation method frequently agrees better with experiments than does the much more sophisticated SCF approach. The reason for this is undoubtedly related to the use by Bates and Damgaard of experimental energies. These energies are invariably lower (more tightly bound) than those resulting from the purely theoretical SCF method, which is a guaranteed feature of variational calculations. The discrepancy is due partly to the SCF assumption that the inner closed shells are spherically symmetric. In fact, these inner shells are polarized by the presence of the valence particle, which causes an attractive force on the valence particle. Biermann[4,5] has shown that this polarization potential is appreciable, and may remove most of the discrepancy between experimental and SCF eigenvalues. This idea, coupled with the well-justified Bates-Damgaard assumptions for monovalent atoms, at least partially explains the excellent results of the Coulomb approximation.

## II. THE NODAL BOUNDARY CONDITION METHOD

The method presented here was devised in an effort to obtain a large number of transition probabilities for atoms and ions having two valence electrons. It involves a technique for making some use of experimental energies in order to simplify the problem. Although considerably more complicated than the one-electron situation, in a limited sense this method can be viewed as an extension of the Bates-Damgaard approach to a more complex system.

The two basic assumptions of the Bates-Damgaard method are that the valence electron moves in a Coulomb field and that its eigenvalue is the experimental term value. Neither approximation is valid, however, for more complex atoms. A valence particle then does not move most of the time in a Coulomb field, and its eigenvalues are not necessarily close to experimental term values, due to the adjustment in position of other valence electrons. Nevertheless, the implications of the two assumptions for monovalent atoms is important for the treatment of more complicated situations. The Coulomb field approximation means that the valence electron wave function is mostly outside the electron core. The eigenvalue approximation implies that the core is nearly unaffected by the position of the valence elec-

tron. These facts are about equally valid for atoms with two electrons outside closed shells. They provide one of the motivations for the nodal boundary condition method.

It will first be established that the inner nodes of many valence radial wave functions are insensitive to their eigenvalues. This "nodal stability" is explained in Sec. III. The positions of these nodes can be found for any atom with two electrons outside closed shells by a study of the corresponding ion with a single valence particle, for which the two Bates-Damgaard assumptions are valid. Nodal positions are then used as the inner boundary conditions on the radial wave functions of the Hartree-Fock equations for the two-electron situation. This provides sufficient information to determine eigenvalues and wave functions. Just as in the Bates-Damgaard method, these wave functions are adequate outside the core, but are incorrect for small radii because of our neglect of the true core potential. This inaccuracy is not important in the calculation of the dipole-moment matrix elements, which overwhelmingly stress the contributions at larger radii.

## III. NODAL STABILITY

The nodal boundary condition method depends on the near independence of node positions with energy. For example, the $3s$ ground-state radial wave function of sodium has two nodes. We will make use of the fact that the $4s$, $5s$, $\cdots$ excited states of sodium have the same two inner nodes, the higher levels merely adding on additional loops and nodes at larger radii.

There is nothing special about using the node positions: the slope-to-value ratio of any part of the valence wave function inside the electron core could be used instead. The part of the valence wave functions inside the core (apart from normalization) is almost the same for any degree of excitation of electrons with a given angular momentum.

The idea of nodal stability can be understood, for example, in terms of Schrödinger's equation

$$P''(r) = [V(r) - E]P(r).$$

It is evident that if the potential $V(r)$ is large compared to the eigenvalue $E$, the radial wavefunction $P(r)$ is nearly independent of $E$. A small change in energy of the valence electron, due to excitation, the presence of other electrons, external fields, or other causes, may radically alter the outer parts of the valence function, but the inner nodes remain in place. The nodal boundary condition method leans heavily on their stability. We will use in particular the fact that (for example) the nodes of the single valence $s$-electron function of Ca II are very close to those for the two valence $s$ electrons in Ca I. That is, an atom and its ion have almost identical core potentials.

Before investigating the evidence for nodal stability, it is necessary to consider just how much stability is

[4] L. Biermann, Z. Astrophys. **22**, 157 (1943).
[5] L. Biermann and K. Lübeck, Z. Astrophys. **25**, 325 (1948).

required. The criterion used in all the calculations is that the nodes should be determined sufficiently accurately so that varying their position within the range of possible error produces only a small change in the calculated eigenvalues and oscillator strengths for the two-electron problem.

The first line of evidence for nodal stability comes from all previously calculated Hartree and Hartree-Fock functions. Many atoms and ions, both ground and excited states, have been solved by the full self-consistent field method. We may investigate the node positions for these atoms for electrons of various angular momenta $(s,p,d,\cdots)$. Known results for several atoms and ions having one or two valence electrons are given in Table I. The nodes are all stable to 5% accuracy and most are stable within 2% accuracy.

The second line of evidence for stable nodes, which serves to find the atoms for which the method can be used, and also the node positions themselves, comes from experimental term values for atoms and ions with one valence electron. The Bates-Damgaard or Coulomb approximation is very good for these atoms, so we can calculate the Coulomb functions, identify the node positions, and investigate the nodal stability. For example, we can calculate the ground-state $(3s)$ valence function of first-ionized magnesium, and find the radius of the outermost node. Then we can calculate the excited state functions $4s$, $5s,\cdots$, and compare the node positions. These "Coulomb nodes" are given for several atoms and ions in Table II. The calculations were made by using experimental eigenvalues and integrating Schrödinger's equation numerically, as described in the Appendix.

TABLE I. Energies and node positions from previous SCF calculations.

| Ion | State | s Node | $\epsilon_s$ | $p$ Node | $\epsilon_p$ | Reference |
|---|---|---|---|---|---|---|
| Na I | $3s$ | 1.034 | 0.361 | | | a |
| Na⁻ | $3s^2\,^1S$ | 1.038 | 0.0268 | | | a |
| Mg II | $3s, 3p$ | 0.899 | 1.1055 | 0.953 | 0.780 | b |
| Mg I | $3s^2\,^1S$ | 0.896 | 0.520 | | | c, d |
| | $3s3p\,^1P$ | 0.890 | 0.650 | 0.9545 | 0.2485 | |
| | $3s3p\,^3P$ | 0.896 | 0.6969 | 0.9545 | 0.4297 | |
| | $3s4s\,^3S$ | 0.893 | 0.8420 | | | |
| | $4s$ | 0.877 | 0.1930 | | | |
| Si IV | $3s, 3p$ | 0.709 | 3.275 | 0.698 | 2.639 | e |
| | $4s, 4p$ | 0.685 | 1.538 | 0.672 | 1.319 | |
| | $5s, 5p$ | 0.677 | 0.893 | 0.663 | 0.793 | |
| K I | $4s$ | 0.4733 | 0.2915 | | | a |
| K⁻ | $4s^2\,^1S$ | 0.4721 | 0.02025 | | | a |
| Ca II | $4s, 4p$ | 1.433 | 0.8295 | 1.610 | 0.6193 | f |
| Ca I | $4s^2\,^1S$ | 1.442 | 0.3891 | | | f |
| | $4s4p\,^1P$ | 1.433 | 0.5052 | 1.650 | 0.1720 | |
| | $4s4p\,^3P$ | 1.441 | 0.5177 | 1.622 | 0.3058 | |

ᵃ D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A193**, 299 (1948).
ᵇ L. Biermann and K. Lübeck, Z. Astrophys. **25**, 325 (1948).
ᶜ L. Biermann and E. Trefftz, Z. Astrophys. **26**, 213 (1949).
ᵈ E. Trefftz, Z. Astrophys. **26**, 240 (1949); **28**, 67 (1950).
ᵉ D. R. Hartree, W. Hartree, and M. F. Manning, Phys. Rev. **60**, 857 (1941).
ᶠ D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A164**, 167 (1938).

TABLE II. Energies and node positions for monovalent ions.

| Ion | State | $\epsilon_s$ | Node | State | $\epsilon_p$ | Node |
|---|---|---|---|---|---|---|
| Na I | $3s$ | 0.3778 | 0.9081 | $3p$ | 0.2232 | 1.033 |
| $(2p^63s)$ | $4s$ | 0.1432 | 0.9114 | $4p$ | 0.10194 | 1.033 |
| | $5s$ | 0.07521 | 0.9105 | $5p$ | 0.05843 | 1.031 |
| Mg II | $3s$ | 1.1057 | 0.8360 | $3p$ | 0.7799 | 0.8838 |
| | $4s$ | 0.4692 | 0.8245 | $4p$ | 0.3704 | 0.8673 |
| | $5s$ | 0.2597 | 0.8197 | $5p$ | 0.2170 | 0.8603 |
| Al III | $3s$ | 2.0921 | 0.7560 | $3p$ | 1.6012 | 0.7651 |
| | $4s$ | 0.9418 | 0.7375 | $4p$ | 0.7820 | 0.7416 |
| | $5s$ | 0.5363 | 0.7308 | $5p$ | 0.4650 | 0.7321 |
| K I | $4s$ | 0.3192 | 1.2767 | $4p$ | 0.2005 | 1.6136 |
| $(3p^64s)$ | $5s$ | 0.1275 | 1.3058 | $5p$ | 0.09388 | 1.6327 |
| | $6s$ | 0.0689 | 1.3134 | $6p$ | 0.05475 | 1.6350 |
| Ca II | $4s$ | 0.8730 | 1.2614 | $4p$ | 0.6420 | 1.473 |
| | $5s$ | 0.3974 | 1.2541 | $5p$ | 0.3206 | 1.451 |
| | $6s$ | 0.2286 | 1.2504 | $6p$ | 0.19364 | 1.441 |
| Rb I | $5s$ | 0.3072 | 1.3741 | $5p$ | 0.1910 | 1.8829 |
| $(4p^65s)$ | $6s$ | 0.1236 | 1.4274 | $6p$ | 0.09049 | 1.9083 |
| | $7s$ | 0.06729 | 1.4376 | $7p$ | 0.05318 | 1.9121 |
| Sr II | $5s$ | 0.8111 | 0.0938 | $5p$ | 0.5900 | 1.7684 |
| | $6s$ | 0.3759 | 0.1184 | $6p$ | 0.3009 | 1.7433 |
| | $7s$ | 0.21882 | 0.1267 | $7p$ | 0.18436 | 1.7197 |
| Cs I | $6s$ | 0.2864 | 1.5669 | $6p$ | 0.1811 | 2.1897 |
| $(5p^66s)$ | $7s$ | 0.1175 | 1.6414 | $7p$ | 0.0868 | 2.2327 |
| | $8s$ | 0.06464 | 1.6649 | $8p$ | 0.05145 | 2.2387 |
| Ba II | $6s$ | 0.7357 | 1.6670 | $6p$ | 0.5406 | 2.106 |
| | $7s$ | 0.3495 | 1.6809 | $7p$ | 0.2816 | 2.078 |
| | $8s$ | 0.2066 | 1.6835 | $8p$ | 0.17461 | 2.058 |
| Cu I | $4s$ | 0.5682 | 0.331 | $4p$ | 0.2883 | none |
| $(3d^{10}4s)$ | $5s$ | 0.1749 | 0.423 | $5p$ | 0.1179 | 5.414 |
| | $6s$ | 0.08633 | 0.440 | $6p$ | 0.0672 | 4.665 |
| Zn II | $4s$ | 1.3211 | 0.5972 | $4p$ | 0.8737 | 0.5756 |
| | $5s$ | 0.5147 | 0.6356 | $5p$ | 0.2954 | 0.6286 |
| | $6s$ | 0.2771 | 0.6429 | $6p$ | 0.2275 | 0.6407 |
| Ga III | $4s$ | 2.2584 | 0.6624 | $4p$ | 1.6358 | 0.7015 |
| | $5s$ | 0.9752 | 0.6761 | $5p$ | 0.7894 | 0.7167 |
| | $6s$ | 0.5483 | 0.6799 | $6p$ | no data | $\cdots$ |
| Ag I | $5s$ | 0.5572 | 0.351 | $5p$ | 0.2821 | none |
| $(4d^{10}5s)$ | $6s$ | 0.1691 | 0.490 | $6p$ | 0.1155 | 5.612 |
| | $7s$ | 0.08407 | 0.516 | $7p$ | 0.06394 | 5.247 |
| Cd II | $5s$ | 1.2434 | 0.6717 | $5p$ | 0.8259 | 0.7271 |
| | $6s$ | 0.4867 | 0.7458 | $6p$ | 0.3758 | 0.8136 |
| | $7s$ | 0.2651 | 0.7606 | $7p$ | 0.21817 | 0.8354 |
| In III | $5s$ | 2.0615 | 0.7752 | $5p$ | 1.5138 | 0.880 |
| | $6s$ | 0.9047 | 0.8130 | $6p$ | 0.7351 | 0.912 |
| | $7s$ | 0.5167 | 0.8219 | $7p$ | 0.4116 | 1.180 |
| Au I | $6s$ | 0.6784 | 0.182 | $6p$ | 0.3145 | none |
| $(5d^{10}6s)$ | $7s$ | 0.1817 | 0.353 | $7p$ | 0.1268 | 4.749 |
| | $8s$ | 0.08815 | 0.384 | $8p$ | 0.06931 | 4.323 |
| Hg II | $6s$ | 1.3793 | 0.5481 | $6p$ | 0.8544 | 0.6358 |
| | $7s$ | 0.5066 | 0.6657 | $7p$ | 0.3696 | 0.8753 |
| | $8s$ | 0.2723 | 0.6880 | $8p$ | 0.2167 | 0.8669 |
| Tl III | $6s$ | 2.194 | 0.6968 | $6p$ | 1.5187 | 0.874 |
| | $7s$ | 0.9254 | 0.7699 | $7p$ | 0.7200 | 0.973 |
| | $8s$ | 0.5235 | 0.7897 | $8p$ | no data | $\cdots$ |

Since the Coulomb approximation does not take into account the influence of the core potential on the valence wave functions, the inner node positions of this method cannot agree with SCF results. In fact, for a given eigenvalue, the nodes obtained by the Coulomb approximation will invariably occur at smaller radii than those of a SCF calculation. This situation prevails because the true potential is deeper than the asymptotic Coulomb potential, so the SCF function, which is the same as the Coulomb function for large radii (if the same eigenvalue is assumed), "curves over" more rapidly as it enters the core.

## IV. TWO-ELECTRON WAVE FUNCTIONS AND TRANSITION PROBABILITIES

The calculation of two-electron radial wave functions will now be described. We wish to solve the Hartree-Fock equations for two electrons, obtaining both eigenvalues and eigenfunctions. In order to do this, inner and outer boundary conditions for each function must be specified. The outer boundary condition is simply the requirement that each function approach zero asymptotically for large radii. The inner boundary condition is that each function must pass through the appropriate Coulomb node position, which we have determined by the method previously discussed.

The calculations have been restricted here to the states $(s^2)$ $^1S_0$, $(ss')$ $^1S_0$ and $^3S_1$, $(sp)$ $^1P_1$ and $^3P_{0,1,2}$ which are the simplest to compute. The method can also be applied to other configurations, such as $(sd)$, $(sf)$, $(p^2)$, $(pp')$, $(pd)$, etc.

### A. Location of the Coulomb Nodes

The first step in the calculations is the preparation of a table of Coulomb nodes for the monovalent ion of the divalent atom in which we are interested. These are just the results given in Table II.

### B. The $s^2$ Ground State and Wave Function

The Hartree-Fock equation for an $s^2$ $^1S_0$ state is

$$P''(r) = \left[ \epsilon - \frac{2C}{r} + \frac{2}{r}\int_0^r dr P^2 + 2\int_r^\infty dr\frac{P^2}{r} \right] P(r), \quad (1)$$

where the eigenvalue $\epsilon$ is measured in Ry, and the radius $r$ is in units of the first Bohr radius.[1] $P''(r)$ denotes the second derivative of the radial function $P$ with respect to $r$, and $C$ is the asymptotic charge acting on the two valence particles ($C=2$ for a neutral atom). If the eigenvalue $\epsilon$ is specified, the equation can be integrated inward from large radii, thereby determining the function (and in particular the node positions) corresponding to that eigenvalue. Doing the calculation repeatedly for different $\epsilon$, a table of eigenvalues versus nodes can be constructed, so that knowing the node positions for various atoms (as we do), the corresponding eigenvalues can be found by interpolation. There are, therefore, available two curves of energy versus node for each atom: that from the $s$ states of the monovalent ion, and also the $s^2$ curve just described. The $s^2$ energy and node for the ground state of the divalent atom can then be read from the intersection of these two curves. Finally, knowing the $s^2$ energy, Eq. (1) can be integrated inward as described in the Appendix.

### C. The $sl$ $^1L$ and $^3L$ Excited-State Functions

The solution of the excited-state equations is the most difficult of the calculations. The Hartree-Fock

equations, which must be solved simultaneously, are

$$P_s'' = \left[ \epsilon_s - \frac{2C}{r} + \frac{2}{r}\int_0^r dr P_l^2 + 2\int_r^\infty dr\frac{P_l^2}{r} \right] P_s$$
$$\pm\frac{1}{2l+1}\left[ \frac{2}{r^{l+1}}\int_0^r dr r^l P_s P_l + 2r^l\int_r^\infty dr\frac{P_s P_l}{r^{l+1}} \right] P_l,$$

$$P_l'' = \left[ \epsilon_l - \frac{2C}{r} + \frac{l(l+1)}{r^2} + \frac{2}{r}\int_0^r dr P_s^2 + 2\int_r^\infty dr\frac{P_s^2}{r} \right] P_l$$
$$\pm\frac{1}{2l+1}\left[ \frac{2}{r^{l+1}}\int_0^r dr r^l P_s P_l + 2r^l\int_r^\infty dr\frac{P_s P_l}{r^{l+1}} \right] P_s,$$

(2)

where the plus and minus signs refer to the singlet and triplet states, and $l=0, 1, 2, \cdots$ (restricted in this work to $l=0$ or 1). Again, these functions $P_s$ and $P_l$ are subject to inner and outer boundary conditions, the inner condition being the requirement that each function pass through the appropriate Coulomb node position. The equations are solved by an iterative procedure, described in the Appendix, beginning with trial eigenvalues and eigenfunctions.

### D. Calculation of Oscillator Strengths

The line strength $S$ of a transition is defined to be

$$S = \sum_{m,m'} |\langle\psi_f^{m'}|r|\psi_i^m\rangle|^2, \quad (3)$$

which is the sum over magnetic quantum numbers of the square of the dipole moment matrix elements connecting the initial and final wave functions. If we define also the quantity $g$ by $g=2J_i+1$, where $J_i$ is the total angular momentum of the initial state, we can define the product $gf$ by

$$gf = \tfrac{1}{3}(\Delta E)S, \quad (4)$$

where $f$ is the oscillator strength, $\Delta E$ is the transition energy in rydbergs, and the line-strength $S$ is expressed in units of the first Bohr radius squared.

The angular parts of the matrix elements are easily evaluated and are well known, so we are left with the radial part

$$M_R = \int dr P_s'(r)P_s(r)\int dr P_l(r)P_{l-1}(r)r. \quad (5)$$

The first integral is over the product of the initial and final radial wave functions of the nonjumping valence electron, and the second integral is over the product of the initial and final radial wave functions and the radius $r$ of the jumping electron. Using our calculated wave functions, the integrals can be evaluated numerically by Simpson's rule.

TABLE III. Oscillator strengths.

| Ion | Transition | $f_1 f_2$ | $S$ | $gf$ | Ion | Transition | $f_1 f_2$ | $S$ | $gf$ |
|---|---|---|---|---|---|---|---|---|---|
| He I | $1\,^1S_0-2\,^1P_1$ | 0.500 | 0.499 | 0.259 | Ga II | $5\,^3S_1-5\,^3P_2$ | 5.558 | 51.49 | 2.46 |
|  | $-3\,^1P_1$ | 0.245 | 0.120 | 0.0679 |  | $-5\,^3P_1$ | 5.558 | 30.8 | 1.46 |
|  | $2\,^1S_0-2\,^1P_1$ | $-4.245$ | 18.02 | 0.265 |  | $-5\,^3P_0$ | 5.558 | 10.3 | 0.48 |
| Li II | $2\,^1S_0-2\,^1P_1$ | $-2.559$ | 6.547 | 0.23 | Sr I | $5\,^1S_0-5\,^1P_1$ | 4.018 | 32.29 | 2.12 |
|  | $-3\,^1P_1$ | 1.725 | 2.974 | 0.65 |  | $-6\,^1P_1$ | 1.313 | 3.45 | 0.356 |
|  | $2\,^3S_1-2\,^3P_2$ | $-2.386$ | 9.49 | 0.52 |  | $6\,^1S_0-5\,^1P_1$ | $-0.482$ | 0.233 | 0.0063 |
|  | $-2\,^3P_1$ | $-2.386$ | 5.69 | 0.31 |  | $-6\,^1P_1$ | 16.18 | 261.7 | 2.78 |
|  | $-2\,^3P_0$ | $-2.386$ | 1.90 | 0.104 |  | $6\,^3S_1-5\,^3P_2$ | $-3.326$ | 18.44 | 0.79 |
| Mg I | $3\,^1S_0-3\,^1P_1$ | 2.951 | 17.42 | 1.85 |  | $-5\,^3P_1$ | $-3.326$ | 11.08 | 0.49 |
|  | $-4\,^1P_1$ | 1.002 | 2.01 | 0.30 |  | $-5\,^3P_0$ | $-3.326$ | 3.69 | 0.16 |
|  | $4\,^1S_0-3\,^1P_1$ | $-0.797$ | 0.635 | 0.016 |  | $6\,^3S_1-6\,^3P_2$ | 10.482 | 183.1 | 2.74 |
|  | $-4\,^1P_1$ | 14.41 | 207.7 | 3.68 |  | $-6\,^3P_1$ | 10.482 | 110.0 | 1.61 |
|  | $4\,^3S_1-3\,^3P_2$ | $-2.686$ | 12.03 | 0.70 |  | $-6\,^3P_0$ | 10.482 | 36.7 | 0.54 |
|  | $-3\,^3P_1$ | $-2.686$ | 7.23 | 0.42 | Cd I | $5\,^1S_0-5\,^1P_1$ | 2.709 | 14.69 | 1.95 |
|  | $-3\,^3P_0$ | $-2.686$ | 2.41 | 0.14 |  | $-6\,^1P_1$ | 0.955 | 1.824 | 0.33 |
|  | $4\,^3S_1-4\,^3P_2$ | 8.594 | 123.1 | 2.48 |  | $6\,^1S_0-5\,^1P_1$ | $-1.215$ | 1.478 | 0.043 |
|  | $-4\,^3P_1$ | 8.594 | 73.9 | 1.49 |  | $-6\,^1P_1$ | 14.49 | 209.9 | 4.20 |
|  | $-4\,^3P_0$ | 8.594 | 24.6 | 0.496 |  | $6\,^3S_1-5\,^3P_2$ | $-2.841$ | 13.46 | 0.80 |
| Al II | $3\,^1S_0-3\,^1P_1$ | 2.464 | 12.15 | 2.20 |  | $-5\,^3P_1$ | $-2.841$ | 8.08 | 0.51 |
|  | $-4\,^1P_1$ | 0.273 | 0.149 | 0.048 |  | $-5\,^3P_0$ | $-2.841$ | 2.69 | 0.17 |
|  | $4\,^1S_0-3\,^1P_1$ | $-1.389$ | 1.931 | 0.208 |  | $6\,^3S_1-6\,^3P_2$ | 8.156 | 110.9 | 2.40 |
|  | $-4\,^1P_1$ | 5.926 | 35.12 | 1.23 |  | $-6\,^3P_1$ | 8.156 | 66.6 | 1.41 |
|  | $4\,^3S_1-3\,^3P_2$ | $-1.576$ | 4.14 | 0.67 |  | $-6\,^3P_0$ | 8.156 | 22.2 | 0.47 |
|  | $-3\,^3P_1$ | $-1.576$ | 2.48 | 0.41 | In II | $5\,^1S_0-5\,^1P_1$ | 2.527 | 12.77 | 2.44 |
|  | $-3\,^3P_0$ | $-1.576$ | 0.83 | 0.135 |  | $-6\,^1P_1$ | 0.645 | 0.833 | 0.28 |
|  | $4\,^3S_1-4\,^3P_2$ | 5.798 | 56.02 | 2.41 |  | $6\,^1S_0-5\,^1P_1$ | $-1.449$ | 2.10 | 0.22 |
|  | $-4\,^3P_1$ | 5.798 | 33.6 | 1.45 |  | $-6\,^1P_1$ | 5.741 | 32.96 | 1.27 |
|  | $-4\,^3P_0$ | 5.798 | 11.2 | 0.48 |  | $6\,^3S_1-5\,^3P_2$ | $-1.776$ | 5.255 | 0.77 |
| Ca I | $4\,^1S_0-4\,^1P_1$ | 3.755 | 28.2 | 2.02 |  | $-5\,^3P_1$ | $-1.776$ | 3.16 | 0.48 |
|  | $-5\,^1P_1$ | 1.216 | 2.96 | 0.37 |  | $-5\,^3P_0$ | $-1.776$ | 1.05 | 0.16 |
|  | $5\,^3S_1-4\,^3P_2$ | $-3.054$ | 15.55 | 0.76 |  | $6\,^3S_1-6\,^3P_2$ | 5.461 | 49.7 | 2.19 |
|  | $-4\,^3P_1$ | $-3.054$ | 9.34 | 0.46 |  | $-6\,^3P_1$ | 5.461 | 29.8 | 1.26 |
|  | $-4\,^3P_0$ | $-3.054$ | 3.11 | 0.15 |  | $-6\,^3P_0$ | 5.461 | 9.95 | 0.41 |
|  | $5\,^3S_1-5\,^3P_2$ | 10.02 | 167.4 | 2.56 | Ba I | $6\,^1S_0-6\,^1P_1$ | 4.423 | 39.12 | 2.14 |
|  | $-5\,^3P_1$ | 10.02 | 100.5 | 1.53 |  | $-7\,^1P_1$ | 1.447 | 4.19 | 0.41 |
|  | $-5\,^3P_0$ | 10.02 | 33.5 | 0.51 |  | $7\,^1S_0-6\,^1P_1$ | $-0.366$ | 0.134 | 0.0041 |
| Zn I | $4\,^1S_0-4\,^1P_1$ | 2.500 | 12.50 | 1.77 |  | $-7\,^1P_1$ | 17.50 | 306.2 | 4.01 |
|  | $-5\,^1P_1$ | 0.898 | 1.614 | 0.31 |  | $7\,^3S_1-6\,^3P_2$ | $-3.570$ | 21.24 | 0.81 |
|  | $5\,^1S_0-4\,^1P_1$ | $-1.277$ | 1.631 | 0.045 |  | $-6\,^3P_1$ | $-3.570$ | 12.75 | 0.52 |
|  | $-5\,^1P_1$ | 14.02 | 196.5 | 4.24 |  | $-6\,^3P_0$ | $-3.570$ | 4.25 | 0.18 |
|  | $5\,^3S_1-4\,^3P_2$ | $-2.713$ | 12.27 | 0.77 |  | $7\,^3S_1-7\,^3P_2$ | 11.19 | 208.8 | 3.06 |
|  | $-4\,^3P_1$ | $-2.713$ | 7.35 | 0.47 |  | $-7\,^3P_1$ | 11.19 | 125.3 | 1.77 |
|  | $-4\,^3P_0$ | $-2.713$ | 2.45 | 0.16 |  | $-7\,^3P_0$ | 11.19 | 41.8 | 0.58 |
|  | $5\,^3S_1-5\,^3P_2$ | 7.823 | 102.0 | 2.37 | Hg I | $6\,^1S_0-6\,^1P_1$ | 2.47 | 12.2 | 2.00 |
|  | $-5\,^3P_1$ | 7.823 | 61.2 | 1.42 |  | $-7\,^1P_1$ | 0.897 | 1.609 | 0.35 |
|  | $-5\,^3P_0$ | 7.823 | 20.4 | 0.47 |  | $7\,^1S_0-6\,^1P_1$ | $-1.679$ | 2.818 | 0.084 |
| Ga II | $4\,^1S_0-4\,^1P_1$ | 2.309 | 10.66 | 2.29 |  | $-7\,^1P_1$ | 14.29 | 204.3 | 4.56 |
|  | $-5\,^1P_1$ | 0.382 | 0.292 | 0.107 | Tl II | $6\,^1S_0-6\,^1P_1$ | 2.36 | 11.14 | 2.56 |
|  | $5\,^1S_0-4\,^1P_1$ | $-1.426$ | 2.032 | 0.22 |  | $7\,^1S_0-6\,^1P_1$ | $-1.538$ | 2.365 | 0.23 |
|  | $-5\,^1P_1$ | 5.820 | 33.87 | 1.43 |  | $7\,^3S_1-6\,^3P_2$ | $-2.014$ | 6.758 | 0.89 |
|  | $5\,^3S_1-4\,^3P_2$ | $-1.655$ | 4.57 | 0.75 |  | $-6\,^3P_1$ | $-2.014$ | 4.06 | 0.65 |
|  | $-4\,^3P_1$ | $-1.655$ | 2.74 | 0.46 |  | $-6\,^3P_0$ | $-2.014$ | 1.35 | 0.23 |
|  | $-4\,^3P_0$ | $-1.655$ | 0.92 | 0.15 |  |  |  |  |  |

## V. RESULTS

Altogether, calculations were carried out for thirteen atoms and ions having two valence electrons. The calculations were restricted to $s$ and $p$ wave functions, so that results were obtained for the states $(s^2)\,^1S_0$; $(ss')\,^1S_0$, $^3S_1$; and $(sp)\,^1P_1$, $^3P_{0,1,2}$. The one-electron eigenvalues can be found in the author's doctoral thesis.[6] Table III contains the transition probability results. The first two columns list the ion and the transition involved. Column three gives the total radial matrix element $f_1 f_2$, where $f_1 = \int P_{1'}r P_{l-1} dr$ and $f_2$

[6] T. M. Helliwell, Ph.D. thesis, California Institute of Technology, Pasadena, California, 1963 (unpublished).

$= \int P_s' P_s dr$. Column four gives the line-strength $S$, and column five gives the $gf$ value of the transition. Because of occasional convergence difficulties with the computer programs, not all of the states could be calculated, which accounts for the absence of some states in the tables.

## VI. GENERAL CONCLUSIONS AND FURTHER APPLICATIONS

The nodal boundary condition technique has allowed us to find approximations to the SCF valence functions, by using experimental term values to eliminate the need for computing wave functions for the core electrons. This

TABLE IV. Comparison of $gf$ values with experiment and SCF calculations.

| Atom | Transition | SCF | Present calculation | Experiment |
|---|---|---|---|---|
| He I | $1\,^1S_0-2\,^1P_1$ | 0.276[a] | 0.259 | ... |
| Mg I | $3\,^1S_0-3\,^1P_1$ | 1.67[b] | 1.85 | 1.2[c] |
| | $4\,^3S_1-3\,^3P_0$ | 0.134[b] | 0.14 | 0.164[d] |
| Ca I | $4\,^1S_0-4\,^1P_1$ | 2.2[e], 1.46[f] | 2.02 | 1.49[g] |
| | $4\,^3P_0-5\,^3S_1$ | | 0.154 | 0.162[h] |
| Zn I | $4\,^1S_0-4\,^1P_1$ | | 1.77 | 1.2[i] |
| | $4\,^3P_2-5\,^3S_1$ | | 0.77 | 0.81[j] |
| Sr I | $5\,^1S_0-5\,^1P_1$ | | 2.12 | 1.54[k] |
| Cd I | $5\,^1S_0-5\,^1P_1$ | | 1.95 | 1.2[l] |
| Ba I | $6\,^1S_0-6\,^1P_1$ | | 2.14 | 1.4[k] |

[a] A. W. Weiss, National Bureau of Standards (private communication).
[b] E. Trefftz, Z. Astrophys. 28, 67 (1950).
[c] Yu. I. Ostrovskii, N. P. Penkin, and L. N. Shabanova, Dokl. Akad. Nauk SSSR 120, 66 (1958) [English transl.: Soviet Phys.—Doklady 3, 538 (1958)].
[d] J. A. H. Kersten, and L. S. Ornstein, Physica 8, 1124 (1941).
[e] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) A164, 167 (1938).
[f] E. Trefftz, Z. Astrophys. 29, 287 (1950).
[g] Yu. I. Ostrovskii and N. P. Penkin, Opt. i Spektroskopiya 10, 8 (1961) [English transl.: Opt. Specty. (USSR) 10, 3 (1961)].
[h] K. H. Olsen, P. M. Routly, and R. B. King, Astrophys. J. 130, 688 (1959).
[i] V. K. Prokofiev, Z. Physik 50, 701 (1928).
[j] J. W. Schuttevaer and J. A. Smit, Physica 10, 502 (1943).
[k] Yu. I. Ostrovskii and N. P. Penkin, Opt. i Spektroskopiya 11, 565 (1961) [English transl.: Opt. Specty. (USSR) 11, 307 (1961)].
[l] W. Kuhn, Naturwiss. 14, 48 (1926).

has simplified the problem to the point where several kinds of states can be calculated fairly quickly for a number of atoms and ions. Also it has served as one possible extension of the Bates-Damgaard method which would be interesting to compare with experiment. The wave functions differ from the usual SCF functions in two important respects. They are incorrect for small radii, since the true core potential is neglected. Therefore, the wave functions are useful only for problems in which the outer parts of the function dominate, which is the case for transition probabilities calculated with the help of the dipole-moment matrix element. Also, the nodal boundary condition functions are on the average about 5% more tightly bound than the usual SCF functions. This increase in binding energy is not surprising, since it is also noticed in comparing the Bates-Damgaard functions with SCF functions for monovalent atoms. The experimental binding energies are greater than those calculated by the usual SCF method, which is presumably due in part to the neglect of core polarization and other correlations when the calculations are made.

Some comparisons of our oscillator strengths with previous experiments and SCF calculations are given in Table IV. Work on the types of atoms treated here is far from complete, so that it is difficult to draw very firm conclusions. Ostrovskii and Penkin[7] have recently measured oscillator strengths for the resonance $(s^2\,^1S_0-sp\,^1P_1)$ lines of Mg I, Ca I, Sr I, and Ba I. Our values are about 25% higher than the experiments. Mg I and Ca I have also been calculated by the full SCF method, with $f$ values which are higher still. The best

[7] Yu. I. Ostrovskii and N. P. Penkin, Opt. i Spektroskopiya 11, 565 (1961) [English transl.: Opt. Spectry. 11, 307 (1961)].

theoretical results for these lines are by Trefftz,[8-10] who has calculated the resonance lines of Mg I and Ca I by the SCF method, but including the effects of core polarization and configuration mixing. Her values are well within the experimental errors, since they are lowered from other SCF calculations principally by taking account of the configuration mixing. We may therefore tentatively conclude that for transition-probability accuracy of better than 25%, single-configuration approximations, even of the full SCF method, are inadequate. Nodal boundary condition values appear to be at least as accurate as those of the usual SCF calculations, but neither should be trusted to better than 25%. This error is not excessive for use in most present astrophysical applications.

The first obvious extension of the nodal boundary condition method is to two-electron valence configurations other than $s^2$, $ss'$, or $sp$. These would be interesting in themselves, but they would also be necessary if a configuration-mixing calculation were to be carried out within the framework of the method. Another extension would be to atoms with an $s^2p$ ground-state configuration, such as B I, Al I, and Ga I.

General applications of nodal boundary condition functions include many problems in which the outer parts of valence functions play a dominant role, which would be the case for certain molecules, and for some solid-state problems. Also, inelastic scattering cross sections, using the Born approximation and the dipole approximation, involve the same matrix elements calculated here.

## ACKNOWLEDGMENTS

## APPENDIX

All of the calculations were carried out with the aid of a program written for the IBM-7090 computer. Three different types of problems were considered: the radial Schrödinger equation with a Coulomb field; the Hartree-Fock equation for the $s^2\,^1S_0$ state; and the two coupled Hartree-Fock equations for the $sl\,^1S_0$ state; and the two coupled Hartree-Fock equations for the $^1L_J$ and $^3L_J$ states.

### A. The Schrödinger Equation with a Coulomb Field

The equation to be solved is

$$P''(r) = \left[\epsilon - \frac{2C}{r} + \frac{l(l+1)}{r^2}\right]P(r), \qquad (6)$$

[8] E. Trefftz, Z. Astrophys. 26, 240 (1949).
[9] E. Trefftz, Z. Astrophys. 28, 67 (1950).
[10] E. Trefftz, Z. Astrophys. 29, 287 (1950).

where $C$ is the charge acting on the valence electron ($C=1$ for a neutral atom) and all quantities are in atomic units. We require that the radial wave function $P(r)$ go to zero for large radii. The solution of this equation with a given (experimental) energy produces Coulomb-approximation wave functions. Except for the hydrogen atom, these do not, in general, vanish at the origin. The equation may be solved numerically by integrating inward from large to small radii. Starting values at large radii may be computed from an asymptotic series representation of the Coulomb function, as used by Bates and Damgaard.[3] Obtaining two starting values in this way, the Schrödinger equation is integrated using the first-order relations

$$hP'(r-h/2) \cong P(r) - P(r-h)$$

and

$$hP''(r) \cong P'(r+h/2) - P'(r-h/2),$$

which are sufficiently accurate for the spacings $h$ used ($h \cong 0.05$).

## B. The $(s^2)\ {}^1S_0$ Hartree-Fock Equations

Since the normalizing condition is $\int P^2(r)dr = 1$, Eq. (1) can be converted to the form

$$P''(r) = \left[ \epsilon - \frac{2(C-1)}{r} - \frac{2}{r}\int_r^\infty dr P^2(r) + 2\int_r^\infty dr \frac{P^2(r)}{r} \right] P(r), \quad (7)$$

which is convenient for inward integration. Here again the eigenvalue $\epsilon$ is specified, and the equation is integrated inward in the same way as for the one-electron Schrödinger equation, except for two differences in procedure. First, the two integrals in the equation need to be evaluated at each step, which can be done by Simpson's rule. Second, the equation is nonlinear, so that the solution must satisfy the normalizing condition $\int P^2(r) = 1$ as calculated. The condition is satisfied by calculating $N \equiv \int_0^\infty dr P^2(r)$ after finding $P(r)$, defining new starting values by $P^{new} = P^{old}/\sqrt{N}$, and solving the equation again. This procedure is repeated until the computed function is correctly normalized to within 0.05%, which requires five or six iterations.

## C. The $sl\ {}^1L$ and ${}^3L$ Hartree-Fock Equations

The equations to be solved are

$$P_s''(r) = \mathrm{HART}_s(r)P_s(r) \pm \mathrm{FOCK}_s(r), \quad (8)$$

and

$$P_l''(r) = \mathrm{HART}_l(r)P_l(r) \pm \mathrm{FOCK}_l(r), \quad (9)$$

where the plus and minus signs refer to the singlet and triplet states, respectively; $l = 0, 1, 2, \cdots$; and

$$\mathrm{HART}_s(r) = \left[ \epsilon_s - \frac{2C}{r} + \frac{2}{r}\int_0^r dr P_l^2 + 2\int_r^\infty dr \frac{P_l^2}{r} \right],$$

$$\mathrm{HART}_l(r) = \left[ \epsilon_l - \frac{2C}{r} + \frac{l(l+1)}{r^2} \right. \quad (10\mathrm{a})$$

$$\left. + \frac{2}{r}\int_0^r dr P_s^2 + 2\int_r^\infty dr \frac{P_s^2}{r} \right],$$

$$\mathrm{FOCK}_s(r) = \frac{1}{2l+1}\left[ \frac{2}{r^{l+1}}\int_0^r dr\, r^l P_s P_l \right.$$

$$\left. + 2r^l \int_r^\infty dr \frac{P_s P_l}{r^{l+1}} \right] P_l, \quad (10\mathrm{b})$$

$$\mathrm{FOCK}_l(r) = \frac{1}{2l+1}\left[ \frac{2}{r^{l+1}}\int_0^r dr\, r^l P_s P_l \right.$$

$$\left. + 2r^l \int_r^\infty dr \frac{P_s P_l}{r^{l+1}} \right] P_s.$$

The over-all procedure of solution is to first specify trial eigenvalues $\epsilon_s$ and $\epsilon_l$, and compute trial Coulomb functions $P_s(r)$ and $P_l(r)$, corresponding to these eigenvalues. Then these eigenvalues and functions are used to evaluate $\mathrm{HART}_l(r)$ and $\mathrm{FOCK}_l(r)$, so that the Eq. (9) can be solved numerically, resulting in a new function $P_l$ and new eigenvalue $\epsilon_l$. The new $\epsilon_l$ will, in general, differ from the trial value because $P_l(r)$ is forced to satisfy the inner and outer boundary conditions by varying $\epsilon_l$. Then $\mathrm{HART}_s(r)$ and $\mathrm{FOCK}_s(r)$ can be computed by using the initial trial values for $\epsilon_s$ and $P_s(r)$, but the new calculated $P_l(r)$. Solving Eq. (8) for $P_s$, a new $P_s(r)$ and $\epsilon_s$ are obtained. This iterative procedure is continued until the eigenfunctions and eigenvalues (hopefully) converge.

These $(sl)$ equations were solved by integrating outwards, starting from (given) Coulomb node positions. At large radii, the solution is checked to see if it is approaching zero asymptotically. If not, the eigenvalue is varied until this outer boundary condition *is* satisfied. Finally, after finding the proper eigenvalue, and the radial function past the Coulomb node which has the correct asymptotic form, the equation can be integrated *inward* from the Coulomb node position so as to find the remainder of the function.