Unified relativistic theory for $1s2p\ ^3P_1$-$1s^2\ ^1S_0$ and $1s2p\ ^1P_1$-$1s^2\ ^1S_0$ frequencies and transition rates in heliumlike ions

G. W. F. Drake

Department of Physics, University of Windsor, Windsor, Ontario N9B 3P4, Canada
(Received 17 October 1978)

The aim of this paper is to test a simple method for converting accurate nonrelativistic predictions of atomic properties into accurate relativistic predictions with a minimum of additional computational effort. The method connects smoothly the exact nonrelativistic LS-coupling results appropriate at small Z with the relativistic jj-coupling results appropriate at large Z. For the processes stated in the title, the method appears to offer a significant improvement in accuracy over relativistic Hartree-Fock or random-phase-approximation calculations, particularly in the low and intermediate range of nuclear charge. For large Z, the present results agree well with the relativistic random-phase approximation.

I. INTRODUCTION

The intercombination $2\ ^3P_1^o - 1\ ^1S_0$ electric dipole transition of the helium isoelectronic sequence has now been studied from two distinct points of view. For small nuclear charge Z, where LS coupling is approximately valid, the appropriate starting point is the nonrelativistic two-electron Schrödinger equation together with the Pauli form of the Breit interaction introduced as a first-order perturbation.[1,2] In this picture, the spin-dependent terms in the Breit interaction[3] mix the $2\ ^3P_1^o$ state with all the $n\ ^1P_1^o$ states, which then undergo allowed electric dipole transitions to the ground state.[4] This approach works well up to $Z \simeq 10$, but then begins to break down as mixing between the states $2\ ^3P_1^o$ and $2\ ^1P_1^o$ can no longer be treated as a small perturbation.[5] One should not diagonalize exactly the Breit-Pauli interaction as an alternative to treating it as a first-order perturbation, unless other higher-order relativistic corrections are simultaneously taken into account.

The second point of view uses the relativistic generalization of the random-phase approximation (RRPA) developed by Johnson *et al.*[6,7] This approach works well in the high-Z region ($Z \gtrsim 30$) where j-j coupling is a good approximation, but deteriorates rapidly with decreasing nuclear charge. Rather large empirical correction factors are required for $Z \lesssim 20$ in order to obtain approximate agreement with the low-Z calculations discussed above.[6] No reliable *a priori* calculations are available in the intermediate coupling region $10 \lesssim Z \lesssim 30$ to check the empirical corrections to the RRPA results.

The purpose of this paper is to develop a unified computational scheme which is valid over the entire range of nuclear charge. The scheme is based on the observation that correlation effects are essentially a low-Z phenomenon, while relativistic effects are essentially a high-Z phenomenon. A judicious combination of expansions in powers of Z^{-1} and αZ is used, together with accurate nonrelativistic matrix elements and exact Dirac hydrogenic matrix elements. Since the states $2\ ^3P_1^o$ and $2\ ^1P_1^o$ become strongly coupled by the Breit interaction, we consider together the transitions $2\ ^3P_1^o - 1\ ^1S_0$ and $2\ ^1P_1^o - 1\ ^1S_0$. The results for both transitions reproduce the most accurate nonrelativistic variational calculations in the limit of low Z, and they are close to the RRPA results in the limit of high Z. It seems likely that the present results offer a significant improvement in accuracy, especially in the low and intermediate range of nuclear charge. To the extent that accurate nonrelativistic calculations are available, the method can readily be extended to many-electron systems.

II. THEORY

The aim of this section is to develop a scheme for calculating radiative transition probabilities which makes maximum use of nonrelativistic calculations for energies, and matrix elements of transition operators and the electron-electron interaction. All one-electron higher-order corrections (summed to infinity in powers of αZ) are then included by evaluating the corresponding matrix elements with exact Dirac hydrogenic eigenfunctions.

A. Calculation of wave functions

The major difficulty in calculating accurate wave functions is to obtain an adequate description of the mixing of the LS-coupled $1s2p\ ^3P_1^o$ and $1s2p\ ^1P_1^o$ states. Our approach is to diagonalize exactly the following matrix in the above two-dimensional basis set

$$\underline{H} = (\underline{H}_{NR} + \underline{B}_P)_{LS} + \underline{R}(\underline{H}_D + \underline{V}_{12} + \underline{B})_{jj}\underline{R}^{-1} - \underline{\Delta} , \quad (1)$$

1387

where

$$H_{NR} = -\frac{\hbar^2}{2m}\sum_{i=1}^{2}\left(\nabla_i^2 + \frac{Ze^2}{r_i}\right) + \frac{e^2}{r_{12}} , \qquad (2)$$

$$H_D = \sum_{i=1}^{2}\left(c\vec{\alpha}_i \cdot \vec{p}_i + \beta_i mc^2 - \frac{Ze^2}{r_i}\right) , \qquad (3)$$

$$V_{12} = e^2/r_{12} , \qquad (4)$$

B_P is the Pauli form of the Breit interaction as given in Ref. 3, B is the relativistic form of the Breit interaction as discussed in Appendix A, and R is the $jj \to LS$ recoupling transformation defined by

$$\begin{pmatrix}|1s2p\,{}^3P_1\rangle \\ |1s2p\,{}^1P_1\rangle\end{pmatrix} = R\begin{pmatrix}|1s_{1/2}2p_{1/2},1\rangle \\ |1s_{1/2}2p_{3/2},1\rangle\end{pmatrix} \qquad (5)$$

with

$$R = \frac{1}{\sqrt{3}}\begin{pmatrix}\sqrt{2} & -1 \\ 1 & \sqrt{2}\end{pmatrix} . \qquad (6)$$

The subscripts LS and jj in Eq. (1) denote the coupling scheme in which the matrix elements are evaluated. The LS matrix elements are calculated with accurate nonrelativistic variational eigenfunctions of H_{NR} including correlation, while the jj matrix elements are calculated with antisymmetric products of hydrogenic Dirac bispinors for nuclear charge Z (i.e., the eigenfunctions of H_D). The matrix Δ in (1) is a correction for those parts which are counted twice in the first two terms. Thus, if H_{NR} and B_P are expanded in the form

$$H_{NR} = Z^2\sum_{n=0}^{\infty} H_{NR}^{(n)}Z^{-n} , \qquad (7)$$

$$B_P = \alpha^2 Z^4\sum_{n=0}^{\infty} B_P^{(n)}Z^{-n} , \qquad (8)$$

then

$$\Delta = Z^2(H_{NR}^{(0)} + H_{NR}^{(1)}/Z)_{LS} + \alpha^2 Z^4(B_P^{(0)} + B_P^{(1)}/Z)_{LS} \qquad (9)$$

since these particular contributions are also contained in the jj terms of (1). The matrix H thus contains all contributions of order Z^{2-n}, $\alpha^2 Z^{4-n}$, $\alpha^2 Z^4(\alpha Z)^{2n}$, and $\alpha^2 Z^3(\alpha Z)^{2n}$, $n = 0$, 1, 2, ..., arising from the nonrelativistic Hamiltonian, the hydrogenic approximation for the relativistic Hamiltonian, and the electron-electron interaction including the exchange of a single transverse photon. Not included are the self-interaction and radiative corrections of quantum electrodynamics such as the Lamb shift (of leading order $\alpha^2 Z^4 \times \ln\alpha Z$). Other than these effects, the leading corrections are of order $\alpha^2 Z^2(\alpha Z)^{2n}$, $n = 1$, 2, ..., arising from the combined effects of relativity

and electron correlation on the electron-electron interaction. This is also the order of magnitude for corrections to the electron-electron interaction arising from the exchange of two or more virtual photons.

The eigenvectors of H (labeled by the eigenvalues E_λ) can be written

$$\begin{pmatrix}|E_1\rangle \\ |E_2\rangle\end{pmatrix} = T\begin{pmatrix}|1s2p\,{}^3P_1\rangle \\ |1s2p\,{}^1P_1\rangle\end{pmatrix} \qquad (10)$$

with

$$T = \begin{pmatrix}\cos\theta & \sin\theta \\ -\sin\theta & \cos\theta\end{pmatrix} \qquad (11)$$

and θ is the singlet-triplet mixing angle. In the limit of low Z, $T \to 1$ (LS coupling) since the first term of (1) dominates the sum of the second and third, and $H_{NR} \gg B_P$. In the limit of large Z, $T \to R^{-1}$ (jj coupling) since the second term dominates the sum of the first and third, and $H_D \gg V_{12} + B$. This corresponds to the physical picture that for small Z, relativistic effects are small, and for large Z, the electron-electron interaction is small compared with the relativistic electron-nucleus interaction. As Z varies, T generates a continuous sequence of transformations which tend to the correct limit in both extremes. The $1s2p\,{}^3P_1$ state connects with the $1s_{1/2}2p_{1/2},1$ state and the $1s2p\,{}^1P_1$ state connects with the $1s_{1/2}2p_{3/2},1$ state. Ermalaev and Jones[8] and Sampson et al.[9] also do an exact diagonalization, but their matrix contains only the $(H_P)_{LS}$ term of (1). Their results therefore do not tend to the correct one-electron Dirac limit for large Z. On the other hand, the calculations of Ivanov et al.[10] are based primarily on the $(H)_{jj}$ term of (1), giving inaccurate results for small Z.

The same Eq. (1) is used also for the $1s^2\,{}^1S_0$ ground state, except that now only a single state is involved and the matrices become one dimensional.

B. Calculation of transition matrix elements

For electric dipole transitions, it is convenient to work in the velocity gauge[11](Coulomb gauge) since the correspondence is then closest between the Dirac $e\vec{\alpha} \cdot \vec{A}$ from of the interaction operator and the $e\vec{p} \cdot \vec{A}/mc$ Pauli form. Using notation analogous to that of the previous subsection, the column vector of transition matrix elements to the ground state is

$$\vec{M} = T[(\vec{M}_P)_{LS} + R(\vec{M})_{jj} - \vec{\Lambda}] , \qquad (12)$$

where

$$(\vec{M}_P)_{LS} = \begin{pmatrix}\langle 1s2p\,{}^3P_1^0| M_{ts} |1s^2\,{}^1S_0\rangle \\ \langle 1s2p\,{}^1P_1^0| M_{ss} |1s^2\,{}^1S_0\rangle\end{pmatrix} , \qquad (13)$$

$$\vec{(M)}_{jj} = e \begin{pmatrix} \langle 1s_{1/2}2p_{1/2}, 1| \sum_i \vec{\alpha}_i \cdot \vec{A}_i^* \,| 1s_{1/2}^2, 0\rangle \\ \langle 1s_{1/2}2p_{3/2}, 1| \sum_i \vec{\alpha}_i \cdot \vec{A}_i^* \,| 1s_{1/2}^2, 0\rangle \end{pmatrix}, \quad (14)$$

and the transformation matrices R and T are defined in Sec. II A. $\vec{\Lambda}$ is the double-counting correction term. The Pauli transition operators M_{ts} and M_{ss} for triplet-singlet (ts) and singlet-singlet (ss) transitions, respectively, are in lowest nonvanishing order

$$M_{ss} = e \sum_{j=1,2} \vec{p}_j \cdot \vec{A}_j^* / mc, \quad (15)$$

$$M_{ts} = \sum_{n>2}^{\infty} \frac{B_P |n^1P_1^o\rangle\langle n^1P_1^o| M_{ss}}{E(2^3P_1^o) - E(n^1P_1^o)}$$

$$+ \sum_{\text{all}\,n} \frac{M_{tt}|n^3P_0^e\rangle\langle n^3P_0^e|B_P}{E(1^1S_0) - E(n^3P_0^e)}$$

$$- \frac{e^2}{4m^2c^3} \sum_{j=1,2} \vec{\sigma}_j \cdot \nabla V_j \times \vec{A}_j^*$$

$$- \frac{e^3}{4m^2c^3r_{12}^3} (\vec{\sigma}_1 \cdot \vec{r}_{12} \times \vec{A}_1^* + 1 \leftrightarrow 2), \quad (16)$$

and $M_{tt} = M_{ss}$. Here, $V_j = -Ze/r_j$, $\vec{r}_{12} = \vec{r}_1 - \vec{r}_2$, and $\vec{\sigma}$ is the Pauli spin operator. As discussed previously,[2,12,13] the first two terms of (16) give the contribution from the first-order perturbation corrections due to B_P to the wave functions of the $2^3P_1^o$ and 1^1S_0 states, respectively, and the last two terms are spin-dependent corrections to the transition operator. However, (16) differs from the usual formulation in that the $n=2$ contribution to the first term is excluded since the $2^3P_1^o - 2^1P_1^o$ perturbation mixing is now contained to all orders in the T matrix. Mixing of $2^3P_1^o$ with higher-n states never becomes large enough for higher-order perturbation corrections to be important, at least in the low and intermediate range of Z. For large Z, Eq. (12) reduces to $\vec{M} \simeq \vec{(M)}_{jj}$, and the detailed structure of $\vec{(M_P)}_{LS}$ becomes unimportant.

The correction vector $\vec{\Lambda}$ in (12) subtracts those terms which are counted twice in the first two terms. In this case, $\vec{(M_P)}_{LS}$ can be expanded

$$\vec{(M_P)}_{LS} = \alpha Z \begin{pmatrix} \alpha^2 Z^2 \sum_{n=0}^{\infty} M_{st}^{(n)} Z^{-n} \\ \sum_{n=0}^{\infty} M_{ss}^{(n)} Z^{-n} \end{pmatrix}. \quad (17)$$

Since the leading terms are also contained in R $\vec{(M)}_{jj}$,

$$\vec{\Lambda} = \alpha Z \begin{pmatrix} \alpha^2 Z^2 M_{st}^{(0)} \\ M_{ss}^{(0)} \end{pmatrix}. \quad (18)$$

As in Sec. II A, the most accurate nonrelativistic

matrix elements available are used in the construction of $\vec{(M_P)}_{LS}$, while $\vec{(M)}_{jj}$ is calculated with jj coupled products of hydrogenic Dirac bispinors. In the limit of low Z, $T \to 1$ and $\vec{M} \to \vec{(M_P)}_{LS}$. In the limit of high Z, $T \to R^{-1}$ and $\vec{M} \to \vec{(M)}_{jj}$.

C. Evaluation of matrix elements

Since the calculations cover the entire isoelectronic sequence from $Z=2$ to $Z=120$, it is convenient to expand all the nonrelativistic LS matrix elements in powers of Z^{-1} and then sum the truncated series for each value of Z, provided that sufficient accuracy can be obtained. The expansion coefficients can always be deduced from explicit calculations (or experimental data) if data of sufficient accuracy are available over a range of Z.[14,15] Alternatively, the expansion coefficients can be calculated directly as described previously from correlated variational basis sets.[16-19]

Starting with Eq. (1), all the nonrelativistic eigenvalues in H_{NR} were obtained to seven-figure accuracy or better for all Z by summing the Z^{-1} expansions of Sanders and Scherr[16] as shown in Eq. (5). The leading two terms in the expansion (6) for B_P were calculated exactly by Doyle.[20] The higher-order terms were extracted from the explicit calculations of Accad et al.[21] for the diagonal elements, and Drake and Dalgarno[1] for the off-diagonal elements in the range $2 \leqslant Z \leqslant 10$. For $Z > 6$, the expansions (in a.u.)

$$\langle 2^1P_1^o|B_P|2^1P_1^o\rangle = \alpha^2 Z^4(-0.1432292 + 0.0554031Z^{-1}$$
$$-0.089Z^{-2} + 0.123Z^{-3}), \quad (19a)$$

$$\langle 2^3P_1^o|B_P|2^3P_1^o\rangle = \alpha^2 Z^4(-0.1536458 + 0.130429Z^{-1}$$
$$-0.162Z^{-2} + 0.041Z^{-3}), \quad (19b)$$

$$\langle 2^3P_1^o|B_P|2^1P_1^o\rangle = \alpha^2 Z^4(-0.0147314 + 0.0288508Z^{-1}$$
$$-0.0047Z^{-2} - 0.014Z^{-3}$$
$$+0.0019Z^{-4}) \quad (19c)$$

reproduce the explicit calculations to about four figures or better (five figures for the diagonal elements). For $Z \leqslant 6$, the explicit values given in Table I were used. For the ground state, one can use to sufficient accuracy[22]

$$\langle 1^1S_0|B_P|1^1S_0\rangle = \alpha^2 Z^4(-0.25 + 0.480140Z^{-1}$$
$$-0.636Z^{-2} + 0.453Z^{-3}$$
$$-0.172Z^{-4} + 0.033Z^{-5}) \quad (20)$$

for all Z. The integrals over hydrogenic Dirac bispinors in $(V_{12} + B)_{jj}$ were done analytically for each Z as described in Appendix B. The correction matrix $\underline{\Delta}$ is

$$\underline{\Delta} = Z^2 \begin{pmatrix} -0.625 + 0.22572779Z^{-1} & 0 \\ 0 & -0.625 + 0.25986890Z^{-1} \end{pmatrix}$$

$$+ \alpha^2 Z^4 \begin{pmatrix} -0.1536458 + 0.130429Z^{-1} & -0.0147314 + 0.0288508Z^{-1} \\ -0.0147314 + 0.0288508Z^{-1} & -0.1432292 + 0.0554031Z^{-1} \end{pmatrix}$$

(21a)

for the $2\,^3P_1^o$, $2\,^1P_1^o$ subspace, and

$$\underline{\Delta} = Z^2(-1 + 0.625Z^{-1}) + \alpha^2 Z^4(-0.25 + 0.480140Z^{-1})$$

(21b)

for the ground state.

The transition matrix elements required in Eq. (12) were evaluated in a similar way. In general, the photon vector potential $\vec{A}$ in (14)–(16) is

$$\vec{A} = \eta \hat{e} e^{i\vec{k}\cdot\vec{r}},$$

(22)

where η is a normalization constant, $\hat{e}$ is the unit polarization vector, $\vec{k}$ is the propagation vector ($|\vec{k}| = \omega/c$), and ω is the frequency. Since the components of $(\vec{M}_P)_{LS}$ are to be calculated only in lowest nonvanishing order, we use the long-wavelength approximation

$$\vec{A} \simeq \eta \hat{e}$$

(23)

for electric dipole transitions. The matrix element of M_{ss} can then be expanded (in a.u.)

$$\langle 1s2p\,^1P_1 | M_{ss} | 1s^2\,^1S_0 \rangle = i\eta\alpha Z \sum_{n=0}^{\infty} M_{ss}^{(n)} Z^{-n}.$$

(24)

The expansion coefficients $M_{ss}^{(n)}$ calculated up to ninth order by the direct variation-perturbation method described in Ref. 19 are listed in Table II. The sums yield nonrelativistic oscillator strengths which agree to four figures or better with the ex-

plicit calculations of Schiff et al.[23] and the Z^{-1} expansions of Scherr and Sanders[17] for all $Z \geq 2$.

The corresponding expansions for the matrix elements of the four terms in M_{ts} shown in Eq. (16) were extracted from explicit variational calculations in the range $2 \leq Z \leq 10$. The infinite summations over intermediate states in the first two terms were replaced by discrete variational basis sets as described previously.[1] Collecting together the first and third terms of (16), which are both of order $\alpha^3 Z^3$, the results are

$$\langle 1s2p\,^3P_1^o | M_{ts} | 1s^2\,^1S_0 \rangle$$

$$= i\eta\alpha^3 Z^3(0.040217 + 0.0318/Z - 0.076/Z^2)$$

$$+ i\eta\alpha^3 Z^2(0.01772 - 0.01460/Z)$$

$$+ i\eta\alpha^3 Z^2(-0.0448 + 0.0567/Z - 0.007/Z^2).$$

(25)

These expansions are adequate for $Z > 6$, but for $Z \leq 6$, the directly calculated values in Table III were used.

The second and third terms above correspond to the second and fourth terms of (16). The coefficient of $\alpha^3 Z^3$ in (25) is exactly $\frac{8}{243}\sqrt{2}\,[\frac{11}{24} + \ln(\frac{3}{2})]$. One obtains precisely the same coefficient by expanding directly the hydrogenic Dirac matrix elements $\langle 1s_{1/2}2p_{3/2}, 1 | \vec{\alpha} \cdot \vec{A} | 1s_{1/2}^2, 0 \rangle$ and $\langle 1s_{1/2}2p_{1/2}, 1 | \vec{\alpha} \cdot \vec{A} | 1s_{1/2}^2, 0 \rangle$ in powers of $(\alpha Z)^2$ and transforming back to LS coupling. Thus the lowest-order contribution from mixing with higher-n

TABLE I. Matrix elements of the Breit–Pauli interaction in LS coupling ($\alpha^2 Z^4$ a.u.).

Z	$\langle 2\,^3P_1^o | B_P | 2\,^3P_1^o \rangle$	$\langle 2\,^1P_1^o | B_P | 2\,^1P_1^o \rangle$	$\langle 2\,^3P_1^o | B_P | 2\,^1P_1^o \rangle$
2	−0.1233163 [a]	−0.1275016 [a]	−0.003039 [b]
3	−0.1266020	−0.1309539	−0.006129
4	−0.130512	−0.133230	−0.008023
5	−0.133709	−0.134786	−0.009258
6	−0.136217	−0.135918	−0.010110
7	−0.138199	−0.136779	−0.010746
8	−0.139793	−0.137456	−0.011225
9	−0.141098	−0.138004	−0.011602
10	−0.142182	−0.138456	−0.011908
15			−0.012833
20			−0.013302
25			−0.013586

[a] The values tabulated are $-[E_J/(2\alpha^2 Z^4 R_M) + 1/8]$ where E_J is the relativistic shift in the ionization potential calculated by Accad et al.[21]

[b] Present work, calculated with 50-term variational wave functions.

TABLE II. Expansion coefficients $M_{ss}^{(n)}$ in Eq. (24) for the $1s2p\ ^1P_1^o - 1s^2\ ^1S_0$ transition (in a.u.).

n	$M_{ss}^{(n)}$
0	0.3950617
1	−0.4458974
2	−0.0840397
3	0.0863962
4	0.0602542
5	−0.0308569
6	−0.0583221
7	0.0021106
8	0.0544527
9	0.0384216

TABLE III. Contributions to $\langle 1s2p\ ^3P_1^o | M_{ts} | 1s^2\ ^1S_0 \rangle$ in units of $i\eta\alpha^3$ a.u. The labels $t_1, \ldots, t_4$ refer to the four terms in Eq.(16), respectively.

Z	$(t_1 + t_3)/Z^3$	t_2/Z^2	t_4/Z^2
2	0.03306	0.00876	−0.01737
3	0.04134	0.01240	−0.02647
4	0.04298	0.01393	−0.03103
5	0.04335	0.01476	−0.03374
6	0.04336	0.01528	−0.03556
7	0.04320	0.01564	−0.03686
8	0.04299	0.01590	−0.03783
9	0.04282	0.01609	−0.03858
10	0.04263	0.01624	−0.03920

states in the nonrelativistic LS picture is automatically included in the one-electron Dirac matrix elements. The correction vector for double counting is thus

$$\vec{\Lambda} = i\eta\alpha Z \begin{pmatrix} 0.040217\,\alpha^2 Z^2 \\ 0.395062 \end{pmatrix}. \tag{26}$$

The relativistic matrix elements required for $(\vec{M})_{jj}$ were calculated directly for each Z from the formulas given by Grant.[8] With phases chosen so that $R(\vec{M})_{jj}$ reduces to $(\vec{M})_{LS}$ in the nonrelativistic limit, the matrix elements for electric dipole transitions are

$$\langle 1s_{1/2}2p_{j'}, 1 | \sum_i \vec{\alpha}_i \cdot \vec{A}_i^* | 1s_{1/2}1s_j, 0 \rangle$$

$$= -(-1)^{j'-1/2} \frac{\eta}{\sqrt{6}} [(2j'+1)(2j+1)]^{1/2}$$

$$\times \begin{pmatrix} j' & 1 & j \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix} \bar{M}_{j'j}, \tag{27}$$

where $j = \frac{1}{2}$, $j' = \frac{1}{2}, \frac{3}{2}$, and $\bar{M}_{j'j}$ involves only the radial integrals

$$\bar{M}_{j'j} = i\{[(\kappa_{j'} - \kappa_j)I_{L+1}^+ + 2I_{L+1}^-]/\sqrt{2}$$
$$- \sqrt{2}[(\kappa_{j'} - \kappa_j)I_{L-1}^+ - I_{L-1}^-]\} \tag{28}$$

with

$$I_L^\pm = \int_0^\infty (P_{j'}Q_j \pm Q_{j'}P_j)j_L(\omega r/c)\,dr,$$

$j_L(z)$ is a spherical Bessel function, P and Q are the large and small radial components of the Dirac bispinor as defined by Grant,[11] and κ is the usual Dirac quantum number.

The first two terms in the $(\alpha Z)^2$ expansions of the matrix elements are

$$\langle 1s_{1/2}2p_{1/2}, 1 | \sum_i \vec{\alpha}_i \cdot \vec{A}_i^* | 1s_{1/2}^2, 0 \rangle$$

$$= i\eta\alpha Z (32/81\sqrt{3})[1 - \alpha^2 Z^2(\tfrac{11}{96} - \tfrac{3}{2}\ln 2 + \ln 3)]$$

$$\tag{29}$$

and

$$\langle 1s_{1/2}2p_{3/2}, 1 | \sum_i \vec{\alpha}_i \cdot \vec{A}_i^* | 1s_{1/2}^2, 0 \rangle$$

$$= i\eta\alpha Z (32\sqrt{2}/81\sqrt{3})[1 - \alpha^2 Z^2(\tfrac{11}{48} - \tfrac{5}{4}\ln 2 + \tfrac{3}{4}\ln 3)].$$

$$\tag{30}$$

These expansions are needed to find the exact value of the $\alpha^3 Z^3$ coefficient in (25) in the LS representation.

III. NUMERICAL RESULTS AND DISCUSSION

The absorption oscillator strength f_λ and spontaneous emission rate A_λ are given by (in a.u.)

$$f_\lambda = (2/\alpha^2\eta^2\omega_\lambda)|M_\lambda|^2,$$

$$A_\lambda = \tfrac{2}{3}\omega_\lambda^2 \alpha^3 f_\lambda,$$

where $\lambda = 1, 2$ labels the two eigenvectors of (1) and the M_λ are the two components of $\vec{M}$ obtained from (12). Calculations have been done for all the ions in the range $2 \leqslant Z \leqslant 120$. A selection of the results is given in Table IV (with $\alpha = \frac{1}{137.03608}$).

The values of $\sqrt{2}\tan\theta$ in Table IV measure the degree of LS-jj recoupling that has taken place. It is interesting that the values exceed unity at the high-Z end. This is caused by a reversal in sign of the off-diagonal matrix element in $(V_{12} + B)_{jj}$ at $Z \simeq 112$. The sign reverses because the $F(r_{12})/r_{12}$ and $-G(r_{12})\vec{\alpha}_1 \cdot \vec{\alpha}_2/r_{12}$ contributions to the matrix element (see Appendix B for F and G) are of opposite sign and, as shown in Table V, the latter eventually overtakes the former. Thus, jj coupling in the $n = 2$ basis set is nearly exact at $Z = 112$. For Z in the range 20 to 40, the $\tan\theta$ values are about 1% larger than those calculated by Ermalaev

and Jones,[8] and about 6% larger than the values of Sampson et al.[9] [$\omega(2p)$ in their notation]. For Z in the range 2–10, the values are in close agreement with the previous variational calculations of Schiff et al.[24] and Drake,[25] but differ by up to 4% from the estimates of van den Eynde et

al.[26] derived from screened hydrogenic wave functions.

The transition frequencies are compared with other calculations in Table VI. Agreement with the calculations of Accad et al.[21] is exact to six or more figures for Z in the range 2–9 when their

TABLE IV. Results for radiative transitions from $1s2p\,^3P_1$ and $1s2p\,^1P_1$ to $1s^2\,^1S_0$. Frequencies are in a.u. and rates are in s^{-1}. Numbers in brackets indicate powers of 10.

Z	$\sqrt{2}\tan\theta$	$2\,^3P_1^o - 1\,^1S_0$			$2\,^1P_1^o - 1\,^1S_0$		
		ω_1	f_1	A_1	ω_2	f_2	A_2
2	3.9272(−4)	0.77056	2.774(−8)	1.764(2)	0.77988	0.2762	1.799(9)
3	1.0883(−3)	2.25228	3.289(−7)	1.787(4)	2.28663	0.4565	2.556(10)
4	2.4106(−3)	4.48104	1.857(−6)	3.993(5)	4.54520	0.5512	1.220(11)
5	4.5488(−3)	7.45924	7.082(−6)	4.220(6)	7.55506	0.6084	3.719(11)
6	7.6891(−3)	1.11879(1)	2.107(−5)	2.825(7)	1.13164(1)	0.6462	8.863(11)
7	1.2036(−2)	1.56680(1)	5.300(−5)	1.394(8)	1.58296(1)	0.6730	1.806(12)
8	1.7761(−2)	2.09001(1)	1.175(−4)	5.499(8)	2.10954(1)	0.6928	3.302(12)
9	2.5045(−2)	2.68852(1)	2.369(−4)	1.834(9)	2.71146(1)	0.7079	5.574(12)
10	3.4055(−2)	3.36243(1)	4.424(−4)	5.356(9)	3.38884(1)	0.7196	8.851(12)
11	4.4945(−2)	4.11183(1)	7.764(−4)	1.406(10)	4.14178(1)	0.7289	1.339(13)
12	5.7847(−2)	4.93686(1)	1.294(−3)	3.376(10)	4.97043(1)	0.7362	1.948(13)
13	7.2871(−2)	5.83763(1)	2.061(−3)	7.523(10)	5.87493(1)	0.7419	2.742(13)
14	9.0094(−2)	6.81428(1)	3.159(−3)	1.571(11)	6.85545(1)	0.7461	3.756(13)
15	0.10956	7.86696(1)	4.679(−3)	3.101(11)	7.91218(1)	0.7491	5.022(13)
16	0.13126	8.99584(1)	6.718(−3)	5.822(11)	9.04531(1)	0.7508	6.579(13)
17	0.15515	1.02011(2)	9.376(−3)	1.045(12)	1.02551(2)	0.7512	8.461(13)
18	0.18112	1.14828(2)	1.275(−2)	1.800(12)	1.15417(2)	0.7505	1.071(14)
19	0.20901	1.28413(2)	1.691(−2)	2.987(12)	1.29055(2)	0.7484	1.335(14)
20	0.23861	1.42768(2)	2.193(−2)	4.786(12)	1.43467(2)	0.7452	1.643(14)
21	0.26965	1.57893(2)	2.782(−2)	7.427(12)	1.58656(2)	0.7407	1.997(14)
22	0.30182	1.73792(2)	3.457(−2)	1.118(13)	1.74625(2)	0.7351	2.401(14)
23	0.33481	1.90467(2)	4.215(−2)	1.638(13)	1.91378(2)	0.7284	2.857(14)
24	0.36824	2.07920(2)	5.045(−2)	2.336(13)	2.08918(2)	0.7207	3.369(14)
25	0.40179	2.26153(2)	5.936(−2)	3.251(13)	2.27249(2)	0.7122	3.939(14)
26	0.43511	2.45170(2)	6.874(−2)	4.425(13)	2.46375(2)	0.7030	4.570(14)
27	0.46790	2.64973(2)	7.844(−2)	5.898(13)	2.66300(2)	0.6933	5.265(14)
28	0.49990	2.85566(2)	8.830(−2)	7.712(13)	2.87029(2)	0.6832	6.029(14)
29	0.53089	3.06950(2)	9.818(−2)	9.907(13)	3.08565(2)	0.6730	6.863(14)
30	0.56069	3.29130(2)	0.1079	1.252(14)	3.30914(2)	0.6628	7.773(14)
32	0.61626	3.75891(2)	0.1267	1.918(14)	3.78070(2)	0.6426	9.837(14)
34	0.66605	4.25878(2)	0.1440	2.797(14)	4.28538(2)	0.6234	1.226(15)
36	0.71000	4.79123(2)	0.1595	3.921(14)	4.82363(2)	0.6056	1.509(15)
40	0.78177	5.95529(2)	0.1847	7.017(14)	6.00281(2)	0.5743	2.216(15)
42	0.81060	6.58769(2)	0.1948	9.052(14)	6.64484(2)	0.5607	2.651(15)
45	0.84659	7.60049(2)	0.2070	1.280(15)	7.67514(2)	0.5424	3.422(15)
50	0.89136	9.46383(2)	0.2213	2.123(15)	9.57739(2)	0.5162	5.071(15)
56	0.92747	1.20002(3)	0.2314	3.569(15)	1.21808(3)	0.4893	7.775(15)
60	0.94434	1.38815(3)	0.2352	4.853(15)	1.41226(3)	0.4728	1.010(16)
65	0.95991	1.64587(3)	0.2374	6.888(15)	1.67977(3)	0.4529	1.369(16)
70	0.97115	1.93006(3)	0.2376	9.480(15)	1.97680(3)	0.4332	1.813(16)
74	0.97790	2.17767(3)	0.2366	1.202(16)	2.23738(3)	0.4173	2.237(16)
80	0.98536	2.58544(3)	0.2335	1.672(16)	2.67023(3)	0.3928	3.000(16)
85	0.98982	2.96153(3)	0.2297	2.158(16)	3.07364(3)	0.3715	3.759(16)
90	0.99313	3.37416(3)	0.2248	2.741(16)	3.52102(3)	0.3493	4.638(16)
100	0.99742	4.32754(3)	0.2119	4.250(16)	4.57459(3)	0.3016	6.760(16)
110	0.99971	5.49990(3)	0.1940	6.286(16)	5.91069(3)	0.2487	9.305(16)
112	1.00001	5.76861(3)	0.1897	6.762(16)	6.22360(3)	0.2374	9.847(16)
120	1.00083	7.00214(3)	0.1691	8.881(16)	7.69423(3)	0.1891	1.199(17)

TABLE V. Contributions to the matrix element $\langle\, 1s_{1/2}2p_{1/2},\ 1|\ V_{12}+B\,|\ 1s_{1/2}2p_{3/2},\ 1\rangle$ in Z a.u.

Z	$\langle F(r_{12})/r_{12}\rangle$ [a]	$\langle -G(r_{12})\vec{\alpha}_1\cdot\vec{\alpha}_2/r_{12}\rangle$ [a]	total
20	0.016275	−0.000728	0.015548
40	0.016774	−0.002848	0.013927
60	0.017453	−0.006167	0.011286
80	0.018046	−0.010347	0.007699
100	0.018067	−0.014837	0.003230
110	0.017569	−0.016898	0.000671
112	0.017401	−0.017269	0.000132
115	0.017092	−0.017784	−0.000692
120	0.016388	−0.018525	−0.002137

[a] The functions $F(r_{12})$ and $G(r_{12})$ are defined by Eqs. (A5) and (A6).

singlet-triplet mixing correction[24] is added to their values. (However, for consistency, their mass polarization and Lamb-shift corrections are omitted from the tabulated values.) The contribution from higher-order effects is just noticeable in the sixth figure at $Z=10$. The RRPA[6] and Ivanov et al.[10] transition frequencies are in poor agreement at low Z, where correlation effects are important, but are quite close at intermediate and high Z. A large part of the discrepancy with the results of Ivanov et al. at high Z is accounted for by their omission of the α^2Z^2 terms in (19) and (20). However, there remain irregularities which are difficult to account for. On the other hand, the differences between our frequencies and the RRPA frequencies increase smoothly as α^2Z^2 in the upper range of Z as expected.

A similar comparison for the oscillator strengths is made in Table VII. The disagreements with the Pauli approximation values f_P for the $2\,^3P_1\text{-}1\,^1S_0$ transition in the range $3\leqslant Z\leqslant 10$ are due in part to the growing importance of higher-order relativistic effects in f_1, and in part to the decreasing importance of relativistic corrections to the $1s^2\,^1S_0$ wave function. The latter correction was omitted in the comparison calculations from Ref. 1, but was included in the $Z=2$ transition integral from Ref. 2. The RRPA oscillator strengths up

TABLE VI. Comparison of transition frequencies (in a.u.). Mass polarization and Lamb-shift corrections are uniformly omitted.

Z	$1s2p\,^3P_1^o\text{-}1s^2\,^1S_0$			$1s2p\,^1P_1^o\text{-}1s^2\,^1S_0$		
	ω_1	ω_{other}	ω_{RRPA} [c]	ω_2	ω_{other}	ω_{RRPA} [c]
2	0.770 559	0.770 559 [a]	0.780	0.779 877	0.779 877 [a]	0.797
3	2.252 281	2.252 280	2.256	2.286 627	2.286 626	2.305
4	4.481 040	4.481 040	4.483	4.545 205	4.545 204	4.564
5	7.459 243	7.459 242	7.460	7.555 064	7.555 063	7.574
6	11.187 95	11.187 95	11.188	11.316 36	11.316 35	11.336
7	15.667 96	15.667 96	15.667	15.829 56	15.829 55	15.849
8	20.900 09	20.900 07	20.898	21.095 36	21.095 33	21.115
9	26.885 20	26.885 16	26.883	27.114 62	27.114 57	27.134
10	33.624 26	33.624 16	33.621	33.888 37	33.888 27	33.908
20	142.768	142.760 [b]	142.760	143.467	143.457 [b]	143.483
30	329.130	329.110	329.119	330.914	330.900	330.921
40	595.529	595.488	595.512	600.281	600.258	600.275
50	946.383	946.315	946.357	957.739	957.711	957.718
60	1388.15	1388.05	1388.11	1412.26	1412.23	1412.23
70	1930.06	1929.92	1930.01	1976.80	1976.76	1976.74
80	2585.44	2585.24	2585.38	2670.23	2670.17	2670.14
90	3374.16	3373.82	3374.08	3521.02	3520.92	3520.88
100	4327.54	4326.39	4327.45	4574.59	4574.43	4574.41

[a] Accad et al., Ref. 21.
[b] Ivanov et al., Ref. 10.
[c] Johnson and Lin, Ref. 6.

TABLE VII. Comparison of oscillator strengths with other calculations.

Z	$1s2p\,^3P_1^o - 1s^2\,^1S_0$			$1s2p\,^1P_1^o - 1s^2\,^1S_0$		
	f_1	f_P	f_{RRPA}	f_2	f_{NR}	f_{RRPA}
2	2.774(−8)	2.774(−8) [a]	3.58(−8) [c]	0.2762	0.2762 [d]	0.2518 [f]
3	3.289(−7)	3.322(−7) [b]	3.63(−7)	0.4565	0.4566	0.4438
4	1.857(−6)	1.866(−6)	1.96(−6)	0.5512	0.5516	0.5443
5	7.082(−6)	7.107(−6)	7.32(−6)	0.6084	0.6089	0.6042
6	2.107(−5)	2.116(−5)	2.16(−5)	0.6462	0.6471	0.6435
7	5.300(−5)	5.321(−5)	5.36(−5)	0.6730	0.6742	0.6712
8	1.175(−4)	1.183(−4)	1.19(−4)	0.6928	0.6944	0.6915
9	2.369(−4)	2.393(−4)	2.39(−4)	0.7079	0.7101	0.7070
10	4.424(−4)	4.494(−4)	4.46(−4)	0.7196	0.7226	0.7190
20	0.02193		0.0222	0.7452	0.784 [e]	0.7470
30	0.1079		0.1055	0.6628	0.808	0.6661
40	0.1847		0.1837	0.5743		0.5764
50	0.2213		0.2212	0.5162		0.5175
60	0.2352		0.2357	0.4728		0.4737
70	0.2376		0.2384	0.4332		0.4341
80	0.2335		0.2344	0.3928		0.3937
90	0.2248		0.2259	0.3493		0.3504
100	0.2119		0.2131	0.3016		0.3029

[a] Drake, Ref. 2.

[b] Drake and Dalgarno, Ref. 1. These results do not include the $1s^2\,^1S_0$ wave function perturbation by B_P.

[c] Johnson and Lin, Ref. 6, including their empirical correction for $Z \leq 20$.

[d] Schiff *et al.*, Ref. 23.

[e] A. Dalgarno and E. M. Parkinson, Proc, R. Soc. London Ser. A **301**, 253 (1967).

[f] Johnson and Lin, Ref. 6.

to $Z = 20$ contain an empirical correction factor due to $^1P^o - ^3P^o$ energy splittings which come out too large[6] (i.e., too little mixing). For the same reason, stronger mixing would decrease the RRPA $2\,^1P_1^o - 1\,^1S_0$ oscillator strengths, bringing them into better agreement with the present values. The larger splittings also show up in the RRPA transition frequencies in comparison with ω_1 and ω_2 (see Table VI). However, the corrections made by Johnson and Lin[6] appear to be too large in absolute magnitude by about 5% at $Z \simeq 14$; increasing to about 20% at both smaller and larger Z.[27] The oscillator strengths themselves are in good agreement throughout the intermediate and jj coupling region. The new theoretical decay rates are compared with the experimental data in Table VIII. All the results fall within the experimental error bars, and the overall agreement is not substantially altered by the present values.

It is interesting that the relativistic corrections to the accurate nonrelativistic oscillator strengths of Schiff *et al.*[24] are as large as 0.4% at $Z = 10$. The differences shown in Table VII are due primarily to the dilution of the $2\,^1P_1^o$ state by the $2\,^3P_1^o$ state. For $Z \geq 30$, nonrelativistic calculations are seriously in error, even for allowed transitions.

IV. CONCLUSIONS

The results of this paper for the transition frequencies and oscillator strengths of the helium isoelectronic sequence show that one can easily incorporate relativistic effects into accurate nonrelativistic calculations with a minimum of additional computational effort. The method, as summarized by Eqs. (1) and (12), requires only one- and two-electron integrals over Dirac hydrogenic wave functions, in addition to the nonrelativistic results. The additional computer time is only a few seconds per ion. Since in general it is easier to perform accurate nonrelativistic calculations than accurate relativistic calculations, it may be that the present approach will turn out to be both more economical and more accurate than a priori relativistic calculations for many-electron systems.

ACKNOWLEDGMENT

APPENDIX A: DISCUSSION OF THE BREIT INTERACTION

Mittleman[28] has derived from quantum electrodynamics an expression for the two-body trans-

TABLE VIII. Comparison of theoretical and experimental decay rates (in s^{-1}) for the transition $1s2p\ ^3P_1^o$-$1s^2\ ^1S_0$.

Ion	Theory	Experiment
N^{5+}	1.394(8) [a] 1.41(8) [b]	(1.7 ±0.30)(8) [c]
O^{6+}	5.499(8) [a] 5.56(8) [b]	(5.80±0.50)(8) [d] (6.01±0.33)(8) [e] (6.01±0.42)(8) [f]
F^{7+}	1.834(9) [a] 1.85(9) [b]	(1.77±0.10)(9) [g] (1.77±0.07)(9) [e]
Si^{12+}	1.571(11) [a] 1.58(11) [b]	(1.57±0.08)(11) [h]
S^{14+}	5.822(11) [a] 5.87(11) [b]	(6.37±0.73)(11) [h]

[a] Present calculation.

[b] RRPA with empirical correction, Refs. 6 and 7.

[c] I. A. Sellin, B. L. Donnally, and C. Y. Fan, Phys. Rev. Lett. 21, 717 (1968).

[d] I. A. Sellin, M. Brown, W. W. Smith, and B. Donnally, Phys. Rev. A 2, 1189 (1970).

[e] P. Richard, R. L. Kauffman, F. F. Hopkins, C. W. Woods, and K. A. Jamison, Phys. Rev. Lett. 30, 888 (1973).

[f] C. F. Moore, W. J. Braithwaite, and D. L. Mathews, Phys. Lett. A 44, 199 (1973).

[g] J. R. Mowat, I. A. Sellin, R. S. Peterson, D. J. Pegg, M. D. Brown, and J. R. MacDonald, Phys. Rev. A 8, 145 (1973).

[h] S. L. Varghese, C. L. Cocke, and B. Curnutte, Phys. Rev. A 14, 1729 (1976).

verse-potential matrix valid for both diagonal and off-diagonal matrix elements. Defining two-particle matrix elements by

$$\beta_{nl,\,n'l'} = \int\int d\vec{r}_1\, d\vec{r}_2\, \psi_n^*(\vec{r}_1)\psi_l^*(\vec{r}_2)$$

$$\times\, \beta_{1,2}\psi_{n'}(\vec{r}_1)\psi_{l'}(\vec{r}_2) \qquad (A1)$$

the results can be written in terms of the state-dependent operator

$$\beta_{1,2} = -(e\hbar c)^2[\vec{\alpha}_1\cdot\vec{\alpha}_2\nabla_{12} - (\vec{\alpha}_1\cdot\vec{\nabla}_{12})(\vec{\alpha}_{12}\cdot\vec{\nabla}_{12})]$$

$$\times\, (1/r_{12}E_{n,n'}^2)\sin^2(r_{12}E_{n,n'}/2\hbar c), \qquad (A2)$$

where $E_{n,n'} = E_n - E_{n'}$ and ∇_{12} operates only on the r_{12} part of (A2). The matrix elements of the total two-body interaction, including the Coulomb repulsion, are

$$(V_{12}+B)_{nl,\,n'l'} = (e^2/r_{12})_{nl,\,n'l'} + \beta_{nl,\,n'l'} + \beta_{ln,\,l'n'}. \qquad (A3)$$

For computational purposes, $\beta_{1,2}$ can be rewritten in a more convenient form. Since the ψ's in (A1) are eigenfunctions of the local Dirac Hamiltonian (3), the term $(\vec{\alpha}_1\cdot\vec{\nabla}_{12})(\vec{\alpha}_2\cdot\vec{\nabla}_{12})f(r_{12})$ can be replaced by the double commutator $[H_1, [H_2, f(r_{12})]]/(\hbar c)^2$. After replacing the H's by their

eigenvalues and some further algebra, the total two-body interaction operator becomes

$$V_{12}+B = (e^2/r_{12})[F(r_{12}) - \vec{\alpha}_1\cdot\vec{\alpha}_2 G(r_{12})] \qquad (A4)$$

with

$$F(r_{12}) = 1 - (E_{l,\,l'}/2E_{n,\,n'})(1-\cos\Omega_{n,\,n'})$$

$$- (E_{n,\,n'}/2E_{l,\,l'})(1-\cos\Omega_{l,\,l'}) \qquad (A5)$$

$$G(r_{12}) = \tfrac{1}{2}(\cos\Omega_{n,\,n'} + \cos\Omega_{l,\,l'}) \qquad (A6)$$

and $\Omega_{n,\,n'} = E_{n,\,n'}r_{12}/\hbar c$. For diagonal matrix elements, either $E_{l,\,l'} = E_{n,\,n'} = 0$ (direct term), or $E_{l,\,l'} = -E_{n,\,n'}$ (exchange term). In either case, Eq. (A4) reduces to the familiar form[29]

$$V_{12}+B = (e^2/r_{12})(1 - \vec{\alpha}_1\cdot\vec{\alpha}_2)\cos\Omega_{n,\,n'}. \qquad (A7)$$

For the off-diagonal $1s_{1/2}2p_{1/2}, 1 - 1s_{1/2}2p_{3/2}, 1$ matrix element, it makes little difference whether (A4) or (A7) is used, except at very high Z where severe cancellation takes place (see Table V) and the fine-structure splitting is no longer small. Even here, the off-diagonal element is much smaller than the difference between the diagonal elements in jj coupling, and the changes in the final results are quite small.

As has been pointed out a number of times,[28,30] the Hamiltonian

$$H = H_D(1) + H_D(2) + V_{12} + B \qquad (A8)$$

is not suitable for an exact diagonalization in a complete basis set of Dirac functions because every eigenvalue is degenerate with a continuum of solutions in which one electron drops into a negative energy state. However, the projected Hamiltonian $\Lambda_{++}H\Lambda_{++}$, where Λ_{++} is the positive energy projection operator, has a well-defined eigenvalue spectrum. In the high-Z limit, our Hamiltonian is, in effect, restricted even further to $\tilde{\Lambda}_{++}H\tilde{\Lambda}_{++}$, where $\tilde{\Lambda}_{++}$ projects onto only the $n = 1$ and $n = 2$ positive energy levels.

APPENDIX B: GENERAL FORMULAS FOR RELATIVISTIC TWO-BODY INTEGRALS

This Appendix gives general formulas for the two-body matrix elements of r_{12}^n and $\vec{\alpha}_1\cdot\vec{\alpha}_2 r_{12}^n$, $n \geq -1$. Integrals containing in addition factors of $\cos(\omega r_{12}/c)$ can then be done by expanding the cosine in power series and integrating term by term. Although such integrals can, in principle, be done directly (in terms of complex $_2F_1$ hypergeometric functions), the above procedure leads to simpler integration formulas which are quite efficient to evaluate. Except at very large Z, the first few terms give sufficient accuracy.

The single-particle Dirac eigenfunctions are

$$\psi_{jlM} = \begin{pmatrix} \varphi_{jlM} \\ \chi_{j\bar{l}M} \end{pmatrix}, \tag{B1}$$

with

$$\varphi_{jlM} = iP(r)/r\Omega_{jlM}, \tag{B2}$$

$$\chi_{j\bar{l}M} = -Q(r)/r\Omega_{j\bar{l}M}, \quad \bar{l} = 2j - l, \tag{B3}$$

and

$$\Omega_{jlM} = \sum_{\mu, m} \langle lm\tfrac{1}{2}\mu | jM \rangle Y_l^m(\hat{r})\chi^\mu, \tag{B4}$$

$$\chi^{1/2} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \chi^{-1/2} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

The integrals are done by integrating explicitly over the r_{12} coordinate as discussed in detail in Ref. 31. In this coordinate system, the volume element is

$$d\vec{r}_1 d\vec{r}_2 = r_1 dr_1 r_2 dr_2 r_{12} dr_{12} \sin\theta_1 d\theta_1 d\varphi_1 d\chi, \tag{B5}$$

where θ_1, φ_1 are the polar angles of $\vec{r}_1$, and χ is the angle of rotation of the triangle formed by $\vec{r}_1$, $\vec{r}_2$, and $\vec{r}_{12}$ about the $\vec{r}_1$ direction. The angular integration over θ_1, φ_1, and χ then leaves finite sums of radial integrals over r_1, r_2, and r_{12} with integrands multiplied by Legendre polynomials $P_\lambda(\cos\theta_{12})$. Here $\cos\theta_{12}$ is regarded as a radial function given by

$$\cos\theta_{12} = (r_1^2 + r_2^2 - r_{12}^2)/2r_1 r_2. \tag{B6}$$

With the definition

$$I_\lambda^{(n)}[f(r_1, r_2, r_{12})]$$

$$= \int_0^\infty dr_1 \int_0^\infty dr_2 \int_{|r_1 - r_2|}^{r_1 + r_2} r_{12} dr_{12}$$

$$\times P_\lambda(\cos\theta_{12})r_{12}^n f(r_1, r_2, r_{12}) \tag{B7}$$

for the radial integrals, the reduction of matrix elements to radial integrals in the $\vec{J} = \vec{j}_1 + \vec{j}_2$ coupled representation is of the form

$$\langle j_1'l_1', j_2'l_2'; J'M' | \vec{\alpha}_1 \cdot \vec{\alpha}_2 r_{12}^n | j_1 l_1, j_2 l_2; JM \rangle = \sum_\lambda \{ -c_{\lambda, J}^{(1)}(j_1'l_1', j_2'l_2'; j_1 \bar{l}_1, j_2 \bar{l}_2) I_\lambda^{(n)}(P_1'P_2'Q_1 Q_2)$$

$$+ c_{\lambda, J}^{(1)}(j_1'l_1', j_2'\bar{l}_2'; j_1 \bar{l}_1, j_2 l_2) I_\lambda^{(n)}(P_1'Q_2'Q_1 P_2)$$

$$+ c_{\lambda, J}^{(1)}(j_1'\bar{l}_1', j_2'l_2'; j_1 l_1, j_2 \bar{l}_2) I_\lambda^{(n)}(Q_1'P_2'P_1 Q_2)$$

$$- c_{\lambda, J}^{(1)}(j_1'\bar{l}_1', j_2'\bar{l}_2'; j_1 l_1, j_2 l_2) I_\lambda^{(n)}(Q_1'Q_2'P_1 P_2) \} \tag{B8}$$

and

$$\langle j_1'l_1', j_2'l_2'; J'M' | r_{12}^n | j_1 l_1, j_2 l_2; JM \rangle = \sum_\lambda \{ c_{\lambda, J}^{(0)}(j_1'l_1', j_2'l_2'; j_1 l_1, j_2 l_2) I_\lambda^{(n)}(P_1'P_2'P_1 P_2)$$

$$+ c_{\lambda, J}^{(0)}(j_1'l_1', j_2'\bar{l}_2'; j_1 l_1, j_2 \bar{l}_2) I_\lambda^{(n)}(P_1'Q_2'P_1 Q_2)$$

$$+ c_{\lambda, J}^{(0)}(j_1'\bar{l}_1', j_2'l_2'; j_1 \bar{l}_1, j_2 l_2) I_\lambda^{(n)}(Q_1'P_2'Q_1 P_2)$$

$$+ c_{\lambda, J}^{(0)}(j_1'\bar{l}_1', j_2'\bar{l}_2'; j_1 \bar{l}_1, j_2 \bar{l}_2) I_\lambda^{(n)}(Q_1'Q_2'Q_1 Q_2) \}. \tag{B9}$$

The angular coefficients $c_{\lambda, J}^{(x)}$, $x = 0, 1$, can be derived by a graphical analysis similar to that described in Ref. 31. The result is proportional to a 15-j symbol of the third kind,[32] which decomposes into sums of products of 6-j and 9-j symbols. The 9-j symbols can be rewritten in terms of 3-j symbols with relations given by Brink and Satchler[33] to obtain the final result

$$c_{\lambda, J}^{(x)}(j_1'l_1', j_2'l_2'; j_1 l_1, j_2 l_2)$$

$$= \tfrac{1}{2}\delta_{J', J}\delta_{M', M}(-1)^{j_1 - l_1 + j_2' - l_2' + J + \lambda + 1}[j_1', j_2', j_1, j_2]^{1/2}$$

$$\times \sum_{y = \lambda - x}^{\lambda + x} \begin{Bmatrix} J & j_2' & j_1' \\ y & j_1 & j_2 \end{Bmatrix} \begin{pmatrix} j_1' & j_1 & y \\ \tfrac{1}{2} & -\tfrac{1}{2} & 0 \end{pmatrix} \begin{pmatrix} j_2' & j_2 & y \\ \tfrac{1}{2} & -\tfrac{1}{2} & 0 \end{pmatrix} d_{\lambda, y}^{(x)}, \tag{B10}$$

where

$$d_{\lambda, \lambda \pm 1}^{(1)} = -(-1)^{j_1 - l_1 + j_2 - l_2}(k_1' + k_1 - \tfrac{1}{2} \mp \lambda \mp \tfrac{1}{2})$$

$$\times (k_2' + k_2 - \tfrac{1}{2} \mp \lambda \mp \tfrac{1}{2})/(\tfrac{1}{2} + \lambda \pm \tfrac{1}{2}), \tag{B11}$$

$$d_{\lambda, \lambda}^{(1)} = \frac{2\lambda + 1}{4\lambda(\lambda + 1)}[(2j_1 + 1) + (-1)^{j_1' + j_1 + \lambda}(2j_1' + 1)]$$

$$\times [(2j_2 + 1) + (-1)^{j_2' + j_2 + \lambda}(2j_2' + 1)], \tag{B12}$$

$$d_{\lambda, \lambda}^{(0)} = (-1)^{j_1 - l_1 + j_2 - l_2}(2\lambda + 1), \tag{B13}$$

$k_i = (l_i - j_i)(2j_i + 1)$, and similarly for k_i'. The l_i's are to be replaced throughout by $\bar{l}_i$'s as necessary for integrals containing small components in (B8) and (B9). For the large components, $k_i = \kappa_i$, and for the small components, $k_i = -\kappa_i$. The notation $[a, b, \dots]$ means $(2a + 1)(2b + 1)\cdots$, and the sums over λ in (B8) and (B9) include all nonvanishing contributions.

There remains now the calculation of the radial integrals defined by (B7). Since the Dirac hydro-

genic radial functions are similar in form to the Schrödinger hydrogenic radial functions, except that the powers of r are nonintegral, all necessary integrals are of the form

$$I_\lambda^{(0)}(r_1^a r_2^b r_{12}^{n-1} e^{-\alpha r_1 - \beta r_2})$$

with a and b arbitrary, and n integral. Only the $\lambda = 0$ case need be calculated directly since the $I_1^{(0)}$ follow from the definition (B6), and all the higher $I_\lambda^{(0)}$ are obtainable from recursion relations given in Ref. 31. After some analysis it can be shown that

$$I_0^{(0)}(r_1^a r_2^b r_{12}^{n-1} e^{-\alpha r_1 - \beta r_2}) = \frac{2\Gamma(a+b+n+3)}{n+1} \sum_{i=1}^{n+1}{}' \binom{n+1}{i} \left\{ \left(\frac{\alpha}{\alpha+\beta}\right)^i \frac{{}_2F_1(b+1+i, -a-n-1+i; b+2+i; \beta/(\alpha+\beta))}{(b+1+i)(\alpha+\beta)^{b+1}\alpha^{a+n+2}} \right.$$
$$\left. + \left(\frac{\beta}{\alpha+\beta}\right)^i \frac{{}_2F_1(a+1+i, -b-n-1+i; a+2+i; \alpha/(\alpha+\beta))}{(a+1+i)(\alpha+\beta)^{a+1}\beta^{b+n+2}} \right\},$$

$$a > -2,\ b > -2,\ n \geq 0,\ (a+b) > -3.\quad \text{(B14)}$$

The ${}_2F_1$'s are hypergeometric functions,[34] and $\sum'$ means that only the odd terms are included in the summation. For the integrals required in the present work, the power series expansions of the ${}_2F_1$'s yield numerically accurate values and, except at high Z, are rapidly convergent. If a and

b are non-negative integers, then the power series terminate after a finite number of terms. If a and b are nearly non-negative integers (as is the case for small αZ), then the residual contribution after the first "near-zero" term in the power series expansion is small.

[1]G. W. F. Drake and A. Dalgarno, Astrophys. J. 157, 456 (1969).
[2]G. W. F. Drake, J. Phys. B 9, L169 (1976).
[3]H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Springer-Verlag, Berlin, 1967), p. 181.
[4]This interpretation is strictly applicable only in the dipole *length* formulation where there are no spin-dependent corrections to the transition operator (see Ref. 2). There is also a small contribution from the perturbation of the $1s^2\ ^1S_0$ state by the Breit interaction.
[5]C. Laughlin, J. Phys. B 11, L391 (1978).
[6]W. R. Johnson and C. D. Lin, Phys. Rev. A 14, 565 (1976).
[7]C. D. Lin, W. R. Johnson, and A. Dalgarno, Phys. Rev. A 15, 154 (1977).
[8]A. M. Ermalaev and M. Jones, J. Phys. B 7, 199 (1974).
[9]D. H. Sampson, A. D. Parks, and R. E. H. Clark, Phys. Rev. A 17, 1619 (1978).
[10]L. N. Ivanov, E. P. Ivanova, and U. I. Safranova, J. Quant. Spectrosc. Radiat. Transfer 15, 553 (1975).
[11]I. P. Grant, J. Phys. B 7, 1458 (1974).
[12]G. W. F. Drake, Phys. Rev. A 5, 1979 (1972).
[13]D. L. Lin, Phys. Rev. A 15, 2324 (1977).
[14]C. W. Scherr, J. N. Silverman, and F. A. Matsen, Phys. Rev. 127, 830 (1962).
[15]P. Blanchard and G. W. F. Drake, J. Phys. B 6, 2495 (1973).
[16]F. C. Sanders and C. W. Scherr, Phys. Rev. 181, 84 (1969).
[17]C. W. Scherr and F. C. Sanders, Int. J. Quantum Chem. 2, 29 (1968).
[18]A. Dalgarno and G. W. F. Drake, Chem. Phys. Lett. 3, 349 (1969).
[19]G. W. F. Drake and A. Dalgarno, Phys. Rev. A 1, 1325 (1970); H. Doyle, M. Oppenheimer, and G. W. F. Drake, *ibid.* 5, 26 (1972).
[20]H. T. Doyle, Adv. At. Molec. Phys. 5, 377 (1969).

These matrix elements of $e^2/r_{12} + B$ are given in jj coupling, and must be transformed to LS coupling. Also, the sign of her $1s_{1/2}2p_{1/2}$-$1s_{1/2}2p_{3/2}$ off-diagonal matrix element should be reversed to agree with nonrelativistic calculations. If phases are chosen so that radial functions are positive at the origin, then the sign of the $2p_{1/2}$ function must be reversed in the nonrelativistic limit.
[21]Y. Accad, C. L. Pekeris, and B. Schiff, Phys. Rev. A 4, 516 (1971).
[22]The leading two terms are given in Ref. 20. The remaining terms were extracted from the explicit calculations of C. L. Pekeris, Phys. Rev. 112, 1649 (1958).
[23]B. Schiff, C. L. Pekeris, and Y. Accad, Phys. Rev. A 4, 885 (1971).
[24]B. Schiff, Y. Accad, and C. L. Pekeris, Phys. Rev. A 8, 2272 (1973).
[25]G. W. F. Drake, Phys. Rev. 181, 23 (1969).
[26]R. K. van den Eynde, G. Wiebes, and Th. Niemeyer, Physica 59, 401 (1972).
[27]Use of the present ^1P-^3P splittings as a basis for comparison would yield slightly smaller correction factors and better overall agreement in the oscillator strengths.
[28]M. H. Mittleman, Phys. Rev. A 4, 897 (1971); 5, 2395 (1972).
[29]Reference 3, p. 181; J. B. Mann and W. R. Johnson, Phys. Rev. A 4, 41 (1971).
[30]G. E. Brown and D. G. Ravenhall, Proc. R. Soc. London Ser. A 208, 552 (1951).
[31]G. W. F. Drake, Phys. Rev. A 18, 820 (1978).
[32]E. El Baz and B. Castel, *Graphical Methods of Spin Algebras* (Marcel Dekker, New York, 1972), pp. 111, 112.
[33]D. M. Brink and G. R. Satchler, *Angular Momentum*, 2nd ed. (Clarendon, Oxford, 1968), pp. 144, 145.
[34]M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1965). Their transformation 15.3.3 is useful in obtaining Eq. (B14).