Special Topics on Precision Measurement in Atomic Physics: Lecture 10

Applications to radiative transitions

Instructor: Gordon W.F. Drake, University of Windsor
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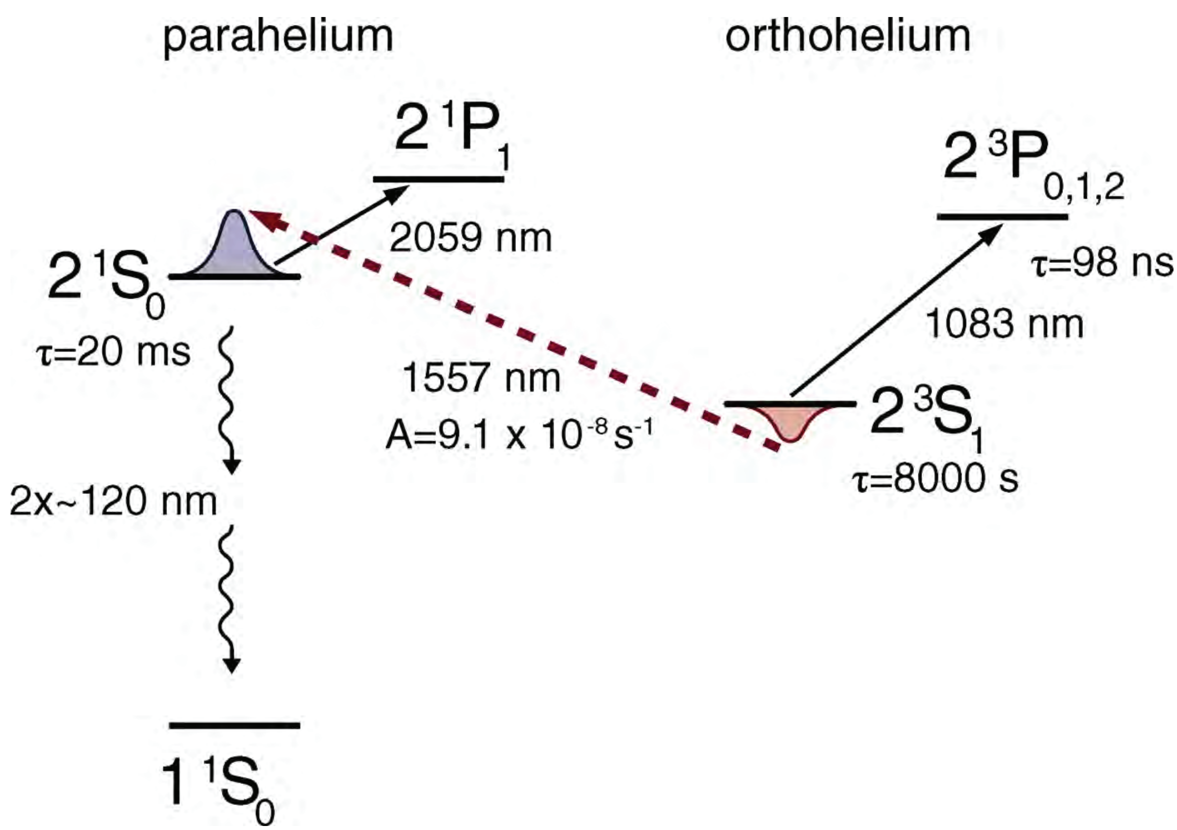
1 Radiative Transitions



R. van Rooij, J. S. Borbely, J. Simonet, M. D. Hoogerland, K. S. E. Eikema,
R. A. Rozendaal, W. Vassen Science 333, 6039 (2011)

1.1 Basic Formulation

In a semiclassical picture, the interaction Hamiltonian with the radiation field is obtained by making the minimal coupling replacements

$$\mathbf{P}_N \rightarrow \mathbf{P}_N - \frac{Ze}{c}\mathbf{A}(\mathbf{R}_N) \tag{1}$$

$$\mathbf{P}_i \rightarrow \mathbf{P}_i + \frac{e}{c}\mathbf{A}_i(\mathbf{R}_i) \tag{2}$$

in the full Hamiltonian in an inertial frame

$$H = \frac{\hbar^2}{2M}P_N^2 + \frac{\hbar^2}{2m}P_1^2 + \frac{\hbar^2}{2m}P_2^2 - \frac{Ze^2}{|\mathbf{X}-\mathbf{x}_1|} - \frac{Ze^2}{|\mathbf{X}-\mathbf{x}_2|} + \frac{e^2}{|\mathbf{x_1}-\mathbf{x}_2|} \tag{3}$$

where

$$\mathbf{A}(\mathbf{R}) = c\left(\frac{2\pi\hbar}{\omega\mathcal{V}}\right)^{1/2}\hat{\boldsymbol{\epsilon}}\, e^{i\mathbf{k\cdot R}} \tag{4}$$

is the time-independent part of the vector potential $\mathbf{A}(\mathbf{r},t) = \mathbf{A}(\mathbf{r})e^{-i\omega t} + \text{c.c}$ for a photon of frequency ω, wave vector $\mathbf{k}$, and polarization $\hat{\boldsymbol{\epsilon}} \perp \mathbf{k}$ normalized to unit photon energy $\hbar\omega$ in volume $\mathcal{V}$. The linear coupling terms then yield

$$H_{\text{int}} = -\frac{Ze}{Mc}\mathbf{P}_N\boldsymbol{\cdot}\mathbf{A}(\mathbf{R}_N) + \frac{e}{m_e c}\sum_{i=1}^{2}\mathbf{P}_i\boldsymbol{\cdot}\mathbf{A}(\mathbf{R}_i)\,, \tag{5}$$

and from Fermi's Golden Rule, the decay rate for spontaneous emission from state γ to γ' is

$$w_{\gamma,\gamma'}d\Omega = \frac{2\pi}{\hbar}|\langle\gamma|H_{\text{int}}|\gamma'\rangle|^2\rho_f\,, \tag{6}$$

where

$$\rho_f = \frac{\mathcal{V}\omega^2}{(2\pi c)^3\hbar}d\Omega \tag{7}$$

is the number of photon states with polarization $\hat{\boldsymbol{\epsilon}}$ per unit energy and solid angle $s\Omega$ in the normalization volume $\mathcal{V}$.

In the long wavelength and electric dipole approximations, the factor $e^{i\mathbf{k\cdot R}}$ in Eq. (4) is replaced by unity. After integrating over angles $d\Omega$ and summing over polarizations $\hat{\boldsymbol{\epsilon}}$, the decay rate reduces to

$$w_{\gamma,\gamma'} = \tfrac{4}{3}\alpha\omega_{\gamma,\gamma'}|\langle\gamma|\mathbf{Q}_p|\gamma'\rangle|^2\,, \tag{8}$$

where $\omega_{\gamma',\gamma}$ is the transition frequency and $\mathbf{Q}_p$ is the velocity form of the transition operator

$$\mathbf{Q}_p = \frac{Z}{Mc}\mathbf{P}_N + \frac{1}{m_e c}\sum_{i=1}^{N} P_i \tag{9}$$

for the general case of N electrons. From the commutator

$$[H_0, \mathbf{Q}_r/\hbar\omega_{\gamma,\gamma'}] = \mathbf{Q}_p \tag{10}$$

where H_0 is the field-free Hamiltonian in Eq. (3), the equivalent length form is

$$\mathbf{Q}_r = -\frac{i}{c}\omega_{\gamma,\gamma'}\left(Z\mathbf{R}_N - \sum_{i=1}^{N}\mathbf{R}_i\right) . \tag{11}$$

After transforming to c.m. plus relative coordinates in parallel with the analysis in Lecture 5, the dipole transition operators become

$$\mathbf{Q}_p = \frac{Z_p}{mc}\sum_{i=1}^{N}\mathbf{p}_i\,, \quad \mathbf{Q}_r = \frac{i\omega_{\gamma,\gamma'}}{c}Z_r\sum_{i=1}^{N}\mathbf{r}_i\,, \tag{12}$$

with

$$Z_p = \frac{Zm_e + M}{M}\,, \quad Z_r = \frac{Zm_e + M}{Nm_e + M}\,,$$

and H_0 now contains the H_{mp} term. If Eq. (**??**) is solved exactly for the states $|\gamma\rangle$ and $|\gamma'\rangle$, then the identity

$$\langle\gamma|\mathbf{Q}_p|\gamma'\rangle = \langle\gamma|\mathbf{Q}_r|\gamma'\rangle \tag{13}$$

is satisfied to all orders in m_e/M. For a neutral atom, $N = Z$ and $Z_r = 1$. If the oscillator strength is defined by

$$\begin{aligned} f_{\gamma',\gamma} &= \frac{2m_e\omega_{\gamma',\gamma}}{3\hbar}\left(\frac{Z_r}{Z_p}\right)|\langle\gamma'|\sum_{i=1}^{N}\mathbf{r}_i|\gamma\rangle|^2 \\ &= \frac{2}{3m_e\hbar\omega_{\gamma',\gamma}}\left(\frac{Z_p}{Z_r}\right)|\langle\gamma'|\sum_{i=1}^{N}\mathbf{p}_i|\gamma\rangle|^2 \end{aligned} \tag{14}$$

then the Thomas-Reiche-Kuhn sum rule $\sum_{\gamma'} f_{\gamma',\gamma} = N$ remains valid, independent of m_e/M. The decay rate, summed over final states and averaged over initial states, is

$$\bar{w}_{\gamma,\gamma'} = -\frac{2\alpha\hbar\omega_{\gamma,\gamma'}}{m_e c^2}Z_p Z_r \bar{f}_{\gamma,\gamma'} \tag{15}$$

where $\bar{f}_{\gamma,\gamma'} = -(g_\gamma/g_{\gamma'})\bar{f}_{\gamma',\gamma}$ is the (negative) oscillator strength for photon emission, and g_γ, $g_{\gamma'}$ are the statistical weights of the states.

Equivalence of Length and Velocity Forms

If the Schrödinger equation is solved exactly with mass polarization included in the Hamiltonian, then the equation

$$\langle\gamma|\mathbf{Q}_p|\gamma'\rangle = \langle\gamma|\mathbf{Q}_r|\gamma'\rangle \tag{16}$$

is satisfied exactly, provided that the mass-dependent factors Z_r and Z_p are included.

This generalizes the idea of mass scaling to radiative transitions. If the wave functions are not exact, then the above equivalence of the length (Q_r) and velocity (Q_p) is no longer exactly true. The difference in the matrix elements provides an estimate of the uncertainty. Note that mass-dependent effects come from the mass-polarization term in the Hamiltonian, as well as from the Z_r, Z_p factors.

Einstein A and B Coefficients

As defined here, the quantity $\bar{w}_{\gamma,\gamma'}$ is identical to the Einstein A coefficient, and has dimensions t^{-1}. It is related to the Einstein B coefficients by the usual relations

$$\begin{aligned} \bar{w}_{\gamma,\gamma'} &\equiv A_{\gamma,\gamma'} \\ &= \frac{2\omega_{\gamma,\gamma'}^2}{\pi c^3}\hbar\omega_{\gamma,\gamma'}\,B_{\gamma,\gamma'} \end{aligned} \tag{17}$$

where $B_{\gamma,\gamma'}$ is the cross section for stimulated emission. The cross section for absorption is

$$B_{\gamma',\gamma} = \frac{g_\gamma}{g_{\gamma'}}B_{\gamma,\gamma'}$$

according to the rule of summing over final states and averaging over initial states, with g_γ and $g_{\gamma'}$ being the statistical weights.

1.2 Oscillator Strength Table

The following table provides arrays of nonrelativistic oscillator strengths among various states of helium, including the effects of finite nuclear mass as a separate factor. In the absence of mass polarization, the correction factor would be $(1+\mu/M)^{-1} \simeq 1-\mu/M$. Mass polarization effects are particularly strong for P-states, and for transitions with $\Delta n = 0$.

Oscillator strengths for helium. The factor in brackets gives the finite mass correction, with $y = \mu/M$.

	$1\,^1S$	$2\,^1S$	$3\,^1S$	$4\,^1S$
$2\,^1P$	$0.276\,1647(1-2.282y)$	$0.376\,4403(1+1.255y)$	$-0.145\,4703(1+1.351y)$	$-0.025\,8703(1+$
$3\,^1P$	$0.073\,4349(1-1.789y)$	$0.151\,3417(1-3.971y)$	$0.626\,1931(1+1.234y)$	$-0.307\,5074(1+$
$4\,^1P$	$0.029\,8629(1-1.583y)$	$0.049\,1549(1-3.235y)$	$0.143\,8889(1-4.650y)$	$0.858\,0214(1+$
$5\,^1P$	$0.015\,0393(1-1.474y)$	$0.022\,3377(1-2.967y)$	$0.050\,4714(1-3.764y)$	$0.146\,2869(1-$
$6\,^1P$	$0.008\,6277(1-1.407y)$	$0.012\,1340(1-2.829y)$	$0.024\,1835(1-3.444y)$	$0.052\,7562(1-$
$7\,^1P$	$0.005\,4054(1-1.362y)$	$0.007\,3596(1-2.75y)$	$0.013\,6794(1-3.279y)$	$0.025\,8918(1-$
	$2\,^3S$	$3\,^3S$	$4\,^3S$	$5\,^3S$
$2\,^3P$	$0.539\,0861(1-3.185y)$	$-0.208\,5359(1-3.773y)$	$-0.031\,7208(1-2.819y)$	$-0.011\,3409(1-$
$3\,^3P$	$0.064\,4612(1+5.552y)$	$0.890\,8513(1-2.967y)$	$-0.435\,6711(1-3.362y)$	$-0.067\,6073(1-$
$4\,^3P$	$0.025\,7689(1+3.886y)$	$0.050\,0833(1+7.505y)$	$1.215\,2630(1-2.878y)$	$-0.668\,3003(1-$
$5\,^3P$	$0.012\,4906(1+3.332y)$	$0.022\,9141(1+5.209y)$	$0.044\,2305(1+9.009y)$	$1.530\,6287(1-$
$6\,^3P$	$0.006\,9822(1+3.063y)$	$0.011\,9933(1+4.460y)$	$0.021\,6301(1+6.198y)$	$0.041\,5177(1+$
$7\,^3P$	$0.004\,2990(1+2.908y)$	$0.007\,0772(1+4.092y)$	$0.011\,7754(1+5.292y)$	$0.021\,1003(1+$
	$2\,^1P$	$3\,^1P$	$4\,^1P$	$5\,^1P$
$3\,^1D$	$0.710\,1641(1-0.281y)$	$-0.021\,1401(1+29.947y)$	$-0.015\,3034(1-6.680y)$	$-0.003\,1128(1-$
$4\,^1D$	$0.120\,2704(1-1.307y)$	$0.648\,1049(1+0.435y)$	$-0.040\,0610(1+29.183y)$	$-0.039\,2932(1-$
$5\,^1D$	$0.043\,2576(1-1.681y)$	$0.141\,3027(1-0.566y)$	$0.647\,6679(1+0.817y)$	$-0.057\,3258(1+$
$6\,^1D$	$0.020\,9485(1-1.866y)$	$0.056\,2766(1-0.936y)$	$0.152\,8104(1-0.170y)$	$0.669\,8361(1+$
$7\,^1D$	$0.011\,8970(1-1.975y)$	$0.028\,8961(1-1.127y)$	$0.063\,5953(1-0.538y)$	$0.163\,0272(1+$
$8\,^1D$	$0.007\,4645(1-2.046y)$	$0.017\,0777(1-1.241y)$	$0.033\,6403(1-0.731y)$	$0.069\,3063(1-$
	$2\,^3P$	$3\,^3P$	$4\,^3P$	$5\,^3P$
$3\,^3D$	$0.610\,2252(1-2.029y)$	$0.112\,1004(1+6.653y)$	$-0.036\,9592(1+3.292y)$	$-0.006\,9009(1+$
$4\,^3D$	$0.122\,8469(1-1.001y)$	$0.477\,5938(1-3.059y)$	$0.200\,9498(1+6.368y)$	$-0.088\,3017(1+$
$5\,^3D$	$0.047\,0071(1-0.631y)$	$0.124\,5532(1-2.019y)$	$0.438\,3888(1-3.607y)$	$0.280\,0558(1+$
$6\,^3D$	$0.023\,4692(1-0.449y)$	$0.053\,0093(1-1.631y)$	$0.123\,9414(1-2.555y)$	$0.429\,4411(1-$
$7\,^3D$	$0.013\,5638(1-0.346y)$	$0.028\,1587(1-1.432y)$	$0.055\,2332(1-2.153y)$	$0.125\,2389(1-$
$8\,^3D$	$0.008\,6047(1-0.280y)$	$0.016\,9809(1-1.315y)$	$0.030\,2853(1-1.94y)$	$0.057\,0589(1-$
	$3\,^1D$	$4\,^1D$	$5\,^1D$	$6\,^1D$
$4\,^1F$	$1.015\,0829(1-1.010y)$	$0.002\,4920(1+3.833y)$	$-0.012\,6968(1-0.888y)$	$-0.002\,2631(1-$
$5\,^1F$	$0.156\,8808(1-0.993y)$	$0.886\,1343(1-1.023y)$	$0.004\,6467(1+4.139y)$	$-0.033\,2539(1-$
$6\,^1F$	$0.054\,0508(1-0.984y)$	$0.186\,0576(1-1.001y)$	$0.839\,1374(1-1.031y)$	$0.006\,6028(1+$
$7\,^1F$	$0.025\,6799(1-0.978y)$	$0.072\,3229(1-0.994y)$	$0.196\,3692(1-1.014y)$	$0.826\,9464(1-$
$8\,^1F$	$0.014\,4782(1-0.978y)$	$0.036\,6627(1-0.987y)$	$0.080\,7847(1-1.003y)$	$0.203\,1182(1-$
$9\,^1F$	$0.009\,0730(1-0.977y)$	$0.021\,5401(1-0.975y)$	$0.042\,4256(1-1.000y)$	$0.086\,0955(1-$
	$3\,^3D$	$4\,^3D$	$5\,^3D$	$6\,^3D$
$4\,^3F$	$1.014\,3389(1-0.997y)$	$0.003\,3992(1-2.166y)$	$-0.012\,8084(1-1.042y)$	$-0.002\,2830(1-$
$5\,^3F$	$0.156\,9831(1-1.004y)$	$0.884\,5767(1-0.991y)$	$0.006\,5121(1-2.387y)$	$-0.033\,5369(1-$
$6\,^3F$	$0.054\,1179(1-1.006y)$	$0.186\,0264(1-1.003y)$	$0.837\,0221(1-0.988y)$	$0.009\,3836(1-$
$7\,^3F$	$0.025\,7201(1-1.008y)$	$0.072\,3579(1-1.003y)$	$0.196\,2031(1-0.996y)$	$0.824\,4031(1-$
$8\,^3F$	$0.014\,5037(1-1.009y)$	$0.036\,6936(1-1.004y)$	$0.080\,7712(1-1.00y)$	$0.202\,8407(1-$
$9\,^3F$	$0.009\,0903(1-1.008y)$	$0.021\,5632(1-1.011y)$	$0.042\,4344(1-0.99y)$	$0.086\,0373(1-$

The largest relativistic correction comes from singlet-triplet mixing between states with the same n, L, and J (e.g. $3\,^1D_2$ and $3\,^3D_2$) due to $H_{\rm FS}$. The wave functions obtained by diagonalizing the 2×2 matrices $\mathbf{H}_0+\mathbf{H}_{\rm NFS}+\mathbf{H}_{\rm FS}$ are then

$$\begin{aligned}\Psi(n\,^1L_L) &= \Psi_0(n\,^1L_L)\cos\theta+\Psi_0(n\,^3L_L)\sin\theta\\ \Psi(n\,^3L_L) &= -\Psi_0(n\,^1L_L)\sin\theta+\Psi_0(n\,^3L_L)\cos\theta\,.\end{aligned}$$

Values of $\sin\theta$ are listed in Table 1.2.

Singlet-triplet mixing angles for helium.

State	$\sin\theta$	State	$\sin\theta$	State	$\sin\theta$
2 P	0.000 2783				
3 P	0.000 2558	3 D	0.015 6095		
4 P	0.000 2498	4 D	0.011 3960	4 F	0.604 1024
5 P	0.000 2473	5 D	0.010 1143	5 F	0.549 9291
6 P	0.000 2460	6 D	0.009 5289	6 F	0.518 0737
7 P	0.000 2452	7 D	0.009 2067	7 F	0.498 4184
8 P	0.000 2447	8 D	0.009 0087	8 F	0.485 5768
9 P	0.000 2444	9 D	0.008 8777	9 F	0.476 7620
10 P	0.000 2442	10 D	0.008 7862	10 F	0.470 4595
5 G	0.693 4752				
6 G	0.693 1996	6 H	0.696 2385		
7 G	0.692 9889	7 H	0.696 2377	7 I	0.697 9315
8 G	0.692 8356	8 H	0.696 2372	8 I	0.697 9315
9 G	0.692 7195	9 H	0.696 2374	9 I	0.697 9316
10 G	0.692 6329	10 H	0.696 2353	10 I	0.697 9316
8 K	0.699 1671				
9 K	0.699 1671	9 L	0.700 1089		
10 K	0.699 1671	10 L	0.700 1089	10 M	0.700 8507

The corrected oscillator strengths $\tilde{f}_{\gamma,\gamma'}$ for the singlet (s) and triplet (t) components of a $\gamma \to \gamma'$ transition can then be calculated from the values in the above table according to

$$\begin{aligned}
\tilde{f}^{\rm ss}_{\gamma,\gamma'} &= \omega^{\rm ss}_{\gamma,\gamma'}\left(X^{\rm ss}_{\gamma,\gamma'}\cos\theta_\gamma\cos\theta_{\gamma'} + X^{\rm tt}_{\gamma,\gamma'}\sin\theta_\gamma\sin\theta_{\gamma'}\right)^2 \;, \\
\tilde{f}^{\rm tt}_{\gamma,\gamma'} &= \omega^{\rm tt}_{\gamma,\gamma'}\left(X^{\rm ss}_{\gamma,\gamma'}\sin\theta_\gamma\sin\theta_{\gamma'} + X^{\rm tt}_{\gamma,\gamma'}\cos\theta_\gamma\cos\theta_{\gamma'}\right)^2 \;, \\
\tilde{f}^{\rm st}_{\gamma,\gamma'} &= \omega^{\rm st}_{\gamma,\gamma'}\left(X^{\rm ss}_{\gamma,\gamma'}\cos\theta_\gamma\sin\theta_{\gamma'} - X^{\rm tt}_{\gamma,\gamma'}\sin\theta_\gamma\cos\theta_{\gamma'}\right)^2 \;, \\
\tilde{f}^{\rm ts}_{\gamma,\gamma'} &= \omega^{\rm ts}_{\gamma,\gamma'}\left(X^{\rm ss}_{\gamma,\gamma'}\sin\theta_\gamma\cos\theta_{\gamma'} - X^{\rm tt}_{\gamma,\gamma'}\cos\theta_\gamma\sin\theta_{\gamma'}\right)^2 \;,
\end{aligned}$$

where $X^{\rm ss}_{\gamma,\gamma'} = (f^{\rm ss}_{\gamma,\gamma'}/\omega^{\rm ss}_{\gamma,\gamma'})^{1/2}$, and similarly for $X^{\rm tt}_{\gamma,\gamma'}$. From Eq. (14), $X_{\gamma,\gamma'}$ is proportional to the dipole *length* form of the transition operator, for which there are no spin-dependent relativistic corrections [see G.W.F. Drake, J. Phys. B **9**, L169 (1976) and K. Pachucki, Phys. Rev. A **69**, 052502 (1004)]. The mixing corrections are particularly significant for D–F and F–G transitions, where intermediate coupling prevails. The two-state approximation becomes increasingly accurate with increasing L, but for P-states, where $\sin\theta$ is small, states with $n' \neq n$ must also be included.

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LETTER TO THE EDITOR

Relativistic corrections to spin-forbidden electric-dipole transitions†

G W F Drake‡

Department of Physics, University of Windsor, Windsor, Ontario, Canada N9B 3P4

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Abstract. Theoretical results for spin-forbidden electric-dipole transitions have recently been questioned on the grounds that relativistic corrections to the transition operator were not included. It is shown here that these corrections are automatically included when the transition operator is expressed in the dipole length form. The above criticism of previous dipole-length calculations is therefore unfounded. The 1s2p $^3P_1$–1s^2 $^1S_0$ and 1s2p $^3P_1$–1s2s $^1S_0$ transitions of helium are discussed as specific numerical examples.

There has been much confusion over the years concerning the correct method of evaluating transition matrix elements for spin-forbidden electric-dipole transitions. The earlier work on the subject is reviewed by Goodman and Laurenzi (1968), and it is discussed from a more general point of view by Drake (1972). The spin-forbidden transition 2^3P_1–1^1S_0 in helium-like ions is of particular interest because precise calculations with correlated variational wavefunctions are available (Drake and Dalgarno 1969), which can be compared with the measured decay rates of Sellin *et al* (1968) and Moore *et al* (1973). The purpose of this letter is to comment on some recent criticisms of the above theoretical work, particularly the corrections proposed by Laughlin (1975) to the calculations of Drake and Dalgarno.

The contributions to the transition integral can be divided into an 'indirect' part coming primarily from the spin–orbit mixing of the $^3P_1$ and $^1P_1$ states, and a 'direct' part due to relativistic spin-dependent corrections to the $\boldsymbol{p}\cdot\boldsymbol{A}$ form of the interaction operator. In recent papers, Luc-Koenig (1974) and Laughlin (1975) suggest that the direct part was not included in previous calculations, and Laughlin explicitly adds the direct part to the matrix elements of Drake and Dalgarno to obtain revised transition probabilities. We show here that this procedure is unfounded—in fact, both the indirect and the direct parts are automatically included, *provided that the matrix element is expressed in the* $\hat{\boldsymbol{e}}\cdot\boldsymbol{r}$ (dipole length) *form*. As a consequence, the division into direct and indirect parts is not unique.

As shown by Drake (1972), the lowest-order interaction energy operator responsible for spin-forbidden electric-dipole transitions in the Coulomb gauge is§

$$U = U^{(1)} + U^{(3)} \tag{1}$$

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‡ Alfred P Sloan Foundation Fellow.

§ Equation (26) of Drake (1972) is printed incorrectly. The last term should be multiplied by $\frac{1}{2}$ so that it agrees with (3) overleaf.

$$U^{(1)} = -\frac{e}{mc}(A_1 . p_1 + A_2 . p_2) \tag{2}$$

$$U^{(3)} = -\frac{e^2}{4m^2c^3}\sum_{j=1,2}\sigma_j . \nabla V_j \times A_j - \frac{e^3}{4m^2c^3r_{12}^3}(\sigma_1 . r_{12} \times A_1 + \sigma_2 . r_{21} \times A_2) \tag{3}$$

including corrections up to relative order $(\alpha Z)^2$. Here, $V_j = -Ze/r_j$, $r_{12} = r_1 - r_2$, σ is the Pauli spin operator and, to sufficient accuracy, $A = (2\omega/3c)^{1/2}\hat{e}$, where $\hat{e}$ is the unit photon polarization vector and ω is its frequency. Equation (3) differs from equation (1) of Laughlin only by a term symmetric in the spin operators, which consequently does not contribute to singlet–triplet transitions.

The direct contribution comes from matrix elements of $U^{(3)}$. Both the direct and the indirect parts are included by writing the interaction energy matrix element in the form

$$U_{i-f} = \langle\Phi_f'|U^{(1)} + U^{(3)}|\Phi_i'\rangle \tag{4}$$

correct to terms of $O(\alpha^2Z^2)$, where Φ' is the non-relativistic wavefunction including first-order corrections for spin mixing due to the Breit interaction B (Bethe and Salpeter 1957). Thus Φ' is an eigenfunction of $H_{NR} + B$ up to spin-dependent terms of $O(\alpha^2Z^2)$, where H_{NR} is the non-relativistic Hamiltonian. Using the explicit forms for B and the photon vector potential A, it is easy to show that correct terms of $O(\alpha^2Z^2)$

$$\begin{aligned}\langle\Phi_f'|U^{(1)} + U^{(3)}|\Phi_i'\rangle &= i\alpha(2\omega/3c)^{1/2}\langle\Phi_f'|[\hat{e}.(r_1 + r_2), H_{NR} + B]|\Phi_i'\rangle \\ &= i\alpha(2\omega/3c)^{1/2}(E_i - E_f)\langle\Phi_f'|\hat{e}.(r_1 + r_2)|\Phi_i'\rangle.\end{aligned} \tag{5}$$

Therefore, the contribution from $U^{(3)}$ is automatically included when the matrix element is evaluated in the dipole length form.

As a direct numerical check, the matrix elements in equation (5) were evaluated for the 1s2p $^3P_1$–1s^2 $^1S_0$ and 1s2p $^3P_1$–1s2s $^1S_0$ transitions of helium with the same 50-term correlated variational wavefunctions as used by Drake and Dalgarno. Except for an overall multiplying factor of $-i\alpha^3(2\omega/3c)^{1/2}$, equation (5) for these transitions reduces to (in atomic units)

$$\begin{aligned}\alpha^{-2}\left\langle n^1S_0'\left|\frac{d}{dz_1} + \frac{d}{dz_2}\right|2^3P_1'\right\rangle + \frac{\sqrt{2}}{4}\langle n^1S|Z(z_1/r_1^3 - z_2/r_2^3) + 2(z_1 - z_2)/r_{12}^3|2^3P\rangle \\ = \alpha^{-2}[E(2^3P) - E(n^1S)]\langle n^1S_0'|z_1 + z_2|2^3P_1'\rangle\end{aligned} \tag{6}$$

where the unprimed wavefunctions are the spin-independent eigenfunctions of H_{NR}. The results shown in table 1 demonstrate that equation (6) is correct to within the accuracy of the calculation, whether or not there is a change in the principal quantum number. The degree to which equations (5) or (6) are satisfied is an indication of the accuracy of the wavefunctions similar to the comparison of the 'length' and 'velocity' forms for allowed transitions.

In summary, the procedure employed by Laughlin in modifying the earlier calculations of the 2^3P_1–1^1S_0 transition integral amounts to counting the contribution from $U^{(3)}$ twice. The results of Drake and Dalgarno are therefore substantially correct as they stand, even though the agreement with experiment is not quite as good as one might desire. The small correction shown in table 1 due to spin–orbit mixing between the $^1S_0$ and doubly excited pp′ $^3P_0^e$ states, which was not included by Drake and Dalgarno, becomes less important with increasing Z and is negligible for the heavier helium-like ions.

Table 1. Matrix elements for the 1sns $^1S_0$–1s2p $^3P_1$ transitions of helium†.

$n =$	1	2
$z^{-2}\left\langle n^1S_0 \left\| \frac{d}{dz_1} + \frac{d}{dz_2} \right\| 2^3P_1' \right\rangle$	2·191 (2·156)	−0·2102 (−0·2078)
$\frac{\sqrt{2}Z}{4}\left\langle n^1S \left\| \frac{z_1}{r_1^3} - \frac{z_2}{r_2^3} \right\| 2^3P \right\rangle$	−0·177	0·0122
$\frac{\sqrt{2}}{2}\left\langle n^1S \left\| \frac{z_1 - z_2}{r_{12}^3} \right\| 2^3P \right\rangle$	−0·069	0·0119
Sum of above	1·945	−0·1861
$z^{-2}[E(2^3P) - E(n^1S)] \times \langle n^1S_0' \| z_1 + z_2 \| 2^3P_1' \rangle$	1·949 (1·962)	−0·1857 (−0·1859)

† The entries in the last row differ from the matrix elements calculated by Drake and Dalgarno (1969) since they did not include a small contribution from the mixing of the 1sns $^1S_0$ state with the doubly excited pp′ $^3P_0^e$ states. The values obtained without this correction are given in brackets.

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Extensive calculations of spin-forbidden transitions in helium carried out by Drake and Morton. See

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Also, the *unified method* can be applied to both allowed and spin-changing transitions for intermediate and mnuclear charge. See G.W.F. Drake, "Unified relativistic theory of $1s2p\,{}^3P_1 - 1s2\,{}^1S_0$ and $1s2p\,{}^1P_1 - 1s2\,{}^1S_0$ frequencies and transition rates in helium-like ions," Phys. Rev. A **19**, 1387 (1979).

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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

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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.

TABLE VII. Comparison of oscillator strengths with other calculations.

Z	f_1	$1s2p\,^3P^o_1$–$1s^2\,^1S_0$ f_P	f_{RRPA}	f_2	$1s2p\,^1P^o_1$–$1s^2\,^1S_0$ 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

RADIATIVE TRANSITIONS IN LITHIUM

For this section, we will look directly at the papers

- Z.-C. Yan and G.W.F. Drake *Theoretical lithium* $2\,^2S - 2\,^2P$ *and* $2\,^2P - 3\,^2D$ *oscillator strengths*, Phys. Rev. A **52**, R4316 (1995).
- Z.-C. Yan, M. Tambasco and G.W.F. Drake *Energies and oscillator strengths for lithiumlike ions*, Phys. Rev. A **57**, 1652 (1998).

The second paper contains and estimate of relativistic corrections and comparisons with a high-precision experiment for the lifetime of the $2\,^2P$ state.