

Relativistic CI Studies for Heliumlike Ions

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Abstract

Relativistic CI calculations of energies and wave functions for heliumlike ions starting from the *no-pair* Hamiltonian are described. Applications of the wave functions to evaluate transition amplitudes, hyperfine structures and quenching, two-photon transition rates, and relativistic corrections to polarizabilities are given.

Collaborators

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Outline

- ★ Relativistic CI Calculations - (Why) & How ?
- ★ Transition Amplitudes - (L & V)
- ★ Hyperfine Quenching - (Coherence & Damping)
- ★ Two-Photon Transitions - Energy Spectra
- ★ Polarizabilities - Relativistic Corrections

Point of Departure

One-electron Dirac equation:

$$h_0 \phi_i = \epsilon_i \phi_i$$

Solve the Dirac equation in a background potential. The spectrum consists of electron bound states, scattering states and negative-energy (positron) states.

Many-electron atoms: The *no-pair* Hamiltonian¹ (from QED) is given by

$$H = \sum_i \epsilon_i :a_i^\dagger a_i: + \frac{1}{2} \sum_{ijkl} v_{ijkl} :a_i^\dagger a_j^\dagger a_l a_k: - \sum_{ij} \Delta V_{ij} :a_i^\dagger a_j:$$

where sums are over positive energy states.

¹BROWN, G.E. & RAVENHALL, D.G. 1951 *Proc. R. Soc. London, Ser. A* **208**, 552-559.

CI for He-like Ions – How?

$$\Psi_{ij}(JM) = \sum_{i \leq j} c_{ij} \Phi_{ij}(JM)$$

$$\Phi_{ij}(JM) = \eta_{ij} \sum_{m_i m_j} \langle j_i m_i j_j m_j | JM \rangle a_{i m_i}^\dagger a_{j m_j}^\dagger |0\rangle$$

$$\eta_{ij} = \begin{cases} 1 & i \neq j \\ 1/\sqrt{2} & i = j \end{cases}$$

$$\langle \Psi_{JM} | \Psi_{JM} \rangle = \sum_{i \leq j} c_{ij}^2 = 1$$

$$\begin{aligned} \langle \Psi_{JM} | H | \Psi_{JM} \rangle &= \sum_{i \leq j} (\epsilon_i + \epsilon_j) c_{ij}^2 \\ &+ \sum_{i \leq j, k \leq l} c_{ij} V(ij; kl) c_{kl} \end{aligned}$$

Example: ${}^3P_0^o$ States

Parity: $l_i + l_j$ odd

Angular Momentum: $|j_i - j_j| \leq 0$

$\Rightarrow \kappa_i = -\kappa_j$

ij	$n_i \times n_j$	Size
$n_i s_{1/2} n_j p_{1/2}$	40×40	1600
$n_i p_{3/2} n_j d_{3/2}$	40×40	3200
$n_i d_{5/2} n_j f_{5/2}$	40×40	4800
$n_i f_{7/2} n_j g_{7/2}$	40×40	6400
\vdots	\vdots	\vdots

Restricting to $l \leq 6$ leads to a matrix $H(ij, kl)$ with 1.2544×10^8 elements (1.00352×10^9 bytes). This matrix is dense!

As a practical matter, we use a Davidson's method routine² to solve the eigenvalue problem.

²A. Stathopoulos and C. F. Fischer, Comput. Phys. Commun. **79**, 268 (1994).

Convergence Pattern for 2^3P_0

Heliumlike neon $Z=10$

Configuration	Increment	Sum
$s_{1/2}p_{1/2}$		-10.3299532
$p_{3/2}d_{3/2}$	-0.0020026	-10.3319559
$d_{5/2}f_{5/2}$	-0.0001506	-10.3321065
$f_{7/2}g_{7/2}$	-0.0000258	-10.3321323
$g_{9/2}h_{9/2}$	-0.0000067	-10.3321390
Tail	-0.0000035	-10.3321425
Total		-10.3321425(3)

Comparison with Experiment

Add estimated QED corrections to find:

$2^3P_0 - 2^3S_1$ Energy Interval (cm^{-1})		
Z	CI	Expt.
5	35393.61(3)	35393.627(0.013)
6	43898.7	43899(1)
7	52420.4	52420.0(1.1)
8	60978.7	60978.4(0.5)
9	69590.8	69590.9(3.4)
10	78263.4	78263.2(2.5)
12	95847.7	95850.6(7.3)
14	113809	113807(4)
16	132219	132218(4)
18	151156	151164(9)
26	233471	232558(550)
36	356828	357400(260)
36 [†]	900115	899685(650)
92	252.77eV	260.0(7.9)eV
92*	100.54keV	100.6(0.1)keV

([†]) $2^3P_2 - 2^3S_1$

(*) $2^3P_2 - 1^1S_0$

Transition Amplitudes

Problem:

L-form and V-form transition amplitudes differ!

Example:

Electric Dipole Amplitudes for He-like Sn ($Z=50$)

Transition	$\langle F T I\rangle_l$	$\langle F T I\rangle_v$
$2^3P_0 - 2^3S_1$	0.057636	0.057345
$2^3P_2 - 2^3S_1$	0.133056	0.132655

Differences arise because negative-energy contributions are absent in CI wave function.

Solution:

Add missing negative-energy contributions from a lowest-order QED calculation.

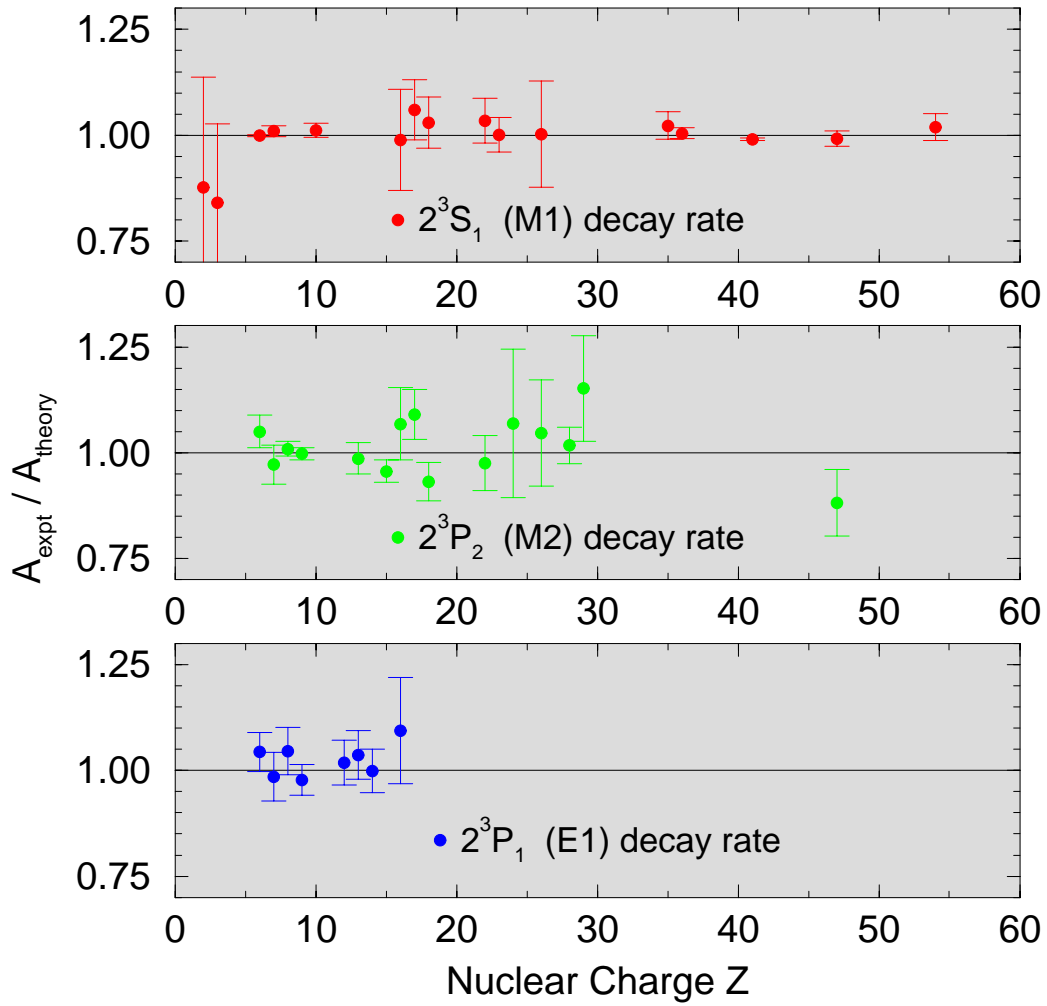
Patch from QED

Add Negative-Energy Contributions from lowest-order QED calculation to CI amplitudes

$Z = 50 \quad 2^2P_0 - 2^2S_1$ transition

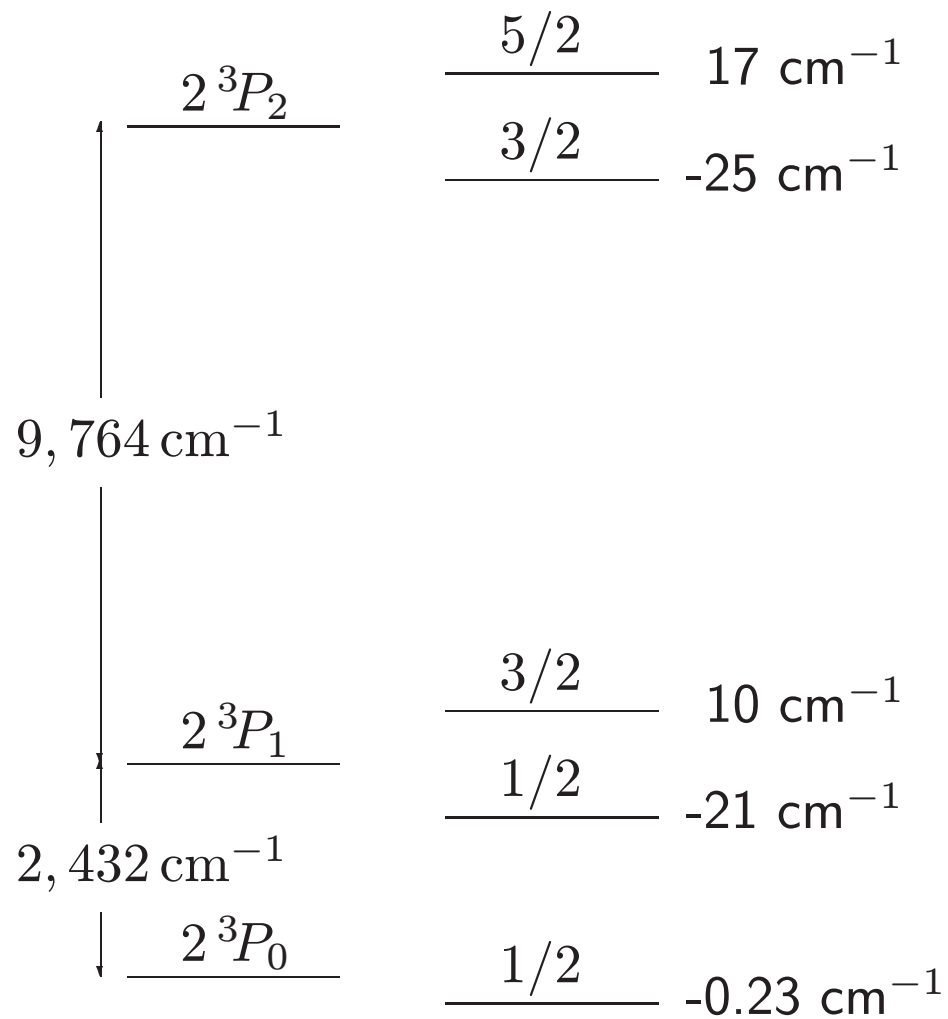
Type	$\langle F Q_1 I \rangle^{(+)}$	$\langle F Q_1 I \rangle^{(-)}$	$\Delta Q(l - v)$
$CI(l)$	0.057636		
$CI(v)$	0.057345		0.000291
$QED(l)$	0.057668	-7×10^{-8}	
$QED(v)$	0.057373	0.000295	0.000000
$CI+QED(l)$	0.057636	-7×10^{-8}	
$CI+QED(v)$	0.057345	0.000295	-0.000004

Measured Transition Rates



Hyperfine Structure

HFS for $^{31}\text{P}^{13+}$ ($I=1/2$)



HFS Theory

$$H_{\text{hf}} = \sum_{\lambda} (-1)^{\lambda} \mathcal{M}_{-\lambda}^{(1)} \mathcal{T}_{\lambda}^{(1)}$$

$$|FM_F\rangle = \sum_{\gamma J} C_{\gamma J}^F \langle IM_I, JM_J | FM_F \rangle |IM_I\rangle |\gamma JM_J\rangle$$

$$(H_0 + H_{\text{hf}})|FM_F\rangle = W_F |FM_F\rangle$$

$$W_F C_{\gamma J}^F = \sum_{\gamma' J'} W_{\gamma J, \gamma' J'}^F C_{\gamma' J'}^F$$

$$\begin{aligned} W_{\gamma J, \gamma' J'}^F &= E_{\gamma J} \delta_{\gamma \gamma'} \delta_{J J'} \\ &+ (-1)^{I+J+F} \left\{ \begin{array}{ccc} I & J & F \\ J' & I & 1 \end{array} \right\} \times \\ &\quad \langle \gamma J || \mathcal{T}^{(1)} || \gamma' J' \rangle \langle I || \mathcal{M}^{(1)} || I \rangle \end{aligned}$$

Energy Matrix for $2P$ States of $^{31}\text{P}^{13+}$

$F=1/2$

	2^3P_0	2^3P_1	2^3P_2	2^1P_1
2^3P_0	0.0000[0]	2.3384[1]	0.0000[0]	-1.4234[1]
2^3P_1	2.3384[1]	2.4114[3]	0.0000[0]	2.2012[1]
2^3P_2	0.0000[0]	0.0000[0]	1.2196[4]	0.0000[0]
2^1P_1	-1.4234[1]	2.2012[1]	0.0000[0]	1.0183[5]
$W_{1/2}$	-2.2880[-1]	2.4116[3]	1.2196[4]	1.0183[5]
	Eigenvector Matrix			
2^3P_0	9.9995[-1]	9.6974[-3]	0.0000[0]	-1.3973[-4]
2^3P_1	-9.6974[-3]	9.9995[-1]	0.0000[0]	2.2138[-4]
2^3P_2	0.0000[0]	0.0000[0]	1.0000[0]	0.0000[0]
2^1P_1	1.4187[-4]	-2.2002[-4]	0.0000[0]	1.0000[0]

Energies for $^{31}\text{P}^{13+}$

$$\mu = 1.1316 \quad I = 1/2$$

	J	F	cm ⁻¹
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Fine Structure

ΔE_{st}	1		101,823
ΔE_{20}	2		12,196
ΔE_{10}	1		2432.2

Hyperfine Structure

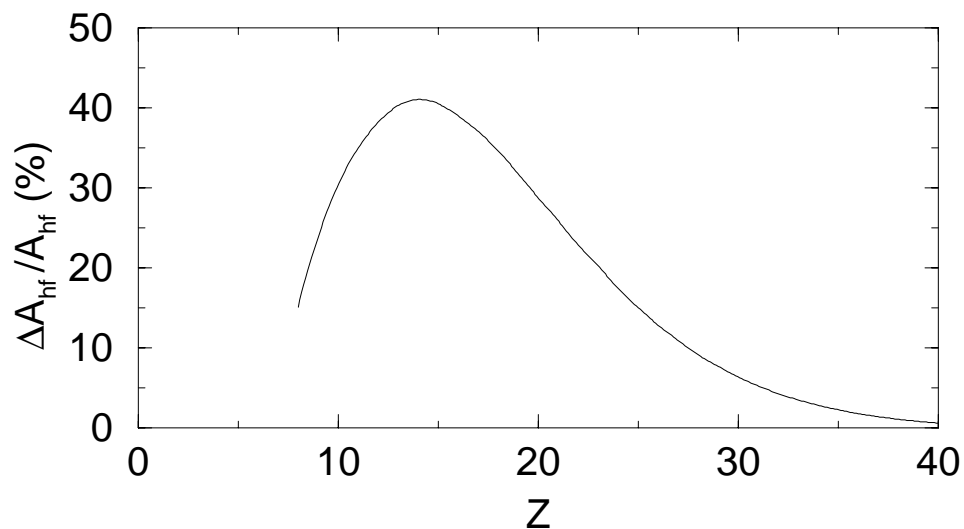
	2	5/2	16.743
	2	3/2	-25.096
	1	3/2	10.382
	1	1/2	-20.597
	0	1/2	-0.229

Quenching & Coherence

Dipole transitions from 2^3P_J state to ground state

$$A_{E1} = \frac{2.02613 \times 10^{18}}{\lambda^3} \times \sum_F \frac{[F]}{3[I][J]} \left| \sum_{\gamma=1,3} C_{\gamma 1}^F \langle 1^1S_0 \| Q_1 \| 2^{\gamma}P_1 \rangle \right|^2$$

Importance of including 2^1P_1 states:

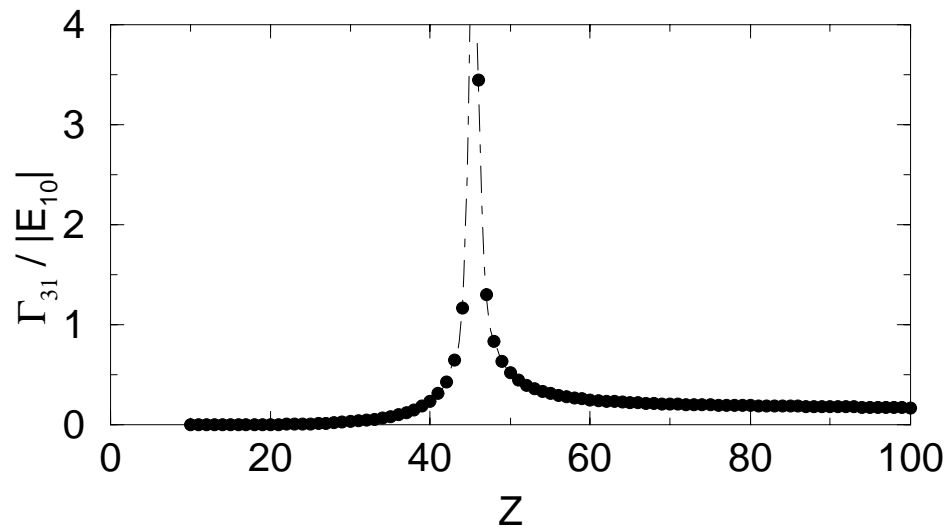


Results

Decay rates (ns^{-1}) in $^{31}\text{P}^{13+}$

Mode	P_2	P_0
$E1 \rightarrow 2\ ^3S_1$	0.0037	0.0409
$E1 \rightarrow 1\ ^1S_0$	0.2214	0.1659
$M2 \rightarrow 1\ ^1S_0$	0.0689	0.0000
A_{tot}	0.2940	0.2068
Expt.	0.298(4)	0.205(4)

Level Widths and Separations



Warning!! ³

Perturbation theory does not work for $\Gamma/2 \geq \Delta E!$

Example: for the 2^3P_0 state of ^{107}Ag ($Z=47$):

$$A_{\text{Pert}} = 384.8 \text{ ns}^{-1}$$

$$A_{\text{Expt}} = 251 \pm 23 \text{ ns}^{-1}$$

³P. Indelicato, F. Parente, and R. Marrus, Phys. Rev. A **40**, 3505 (1989).

Radiation Damping⁴

Wide levels: $\Gamma/2 \geq \Delta E$

$$V_{\text{rd}}|\psi_E\rangle = ie^2 \sum_{kq\lambda} \frac{(k+1)(2k+1)}{k [(2k+1)!!]^2} \times \\ \sum_n k_n^{2J+1} Q_{kq}^{(\lambda)} |\psi_n\rangle \langle \psi_n | Q_{kq}^{(\lambda)\dagger} |\psi_E\rangle$$

$$\langle 2^{\gamma}P_J | V_{\text{rd}} | 2^{\gamma}P_J \rangle = i \frac{\hbar}{2} \sum_{k\lambda} \sum_n A_k^{(\lambda)} (2^{\gamma}P_J \Rightarrow n)$$

$$\langle 2^3P_1 | V_{\text{rd}} | 2^1P_1 \rangle = \\ i \frac{\hbar}{2} \left\{ \frac{4}{9} k_0^3 \langle 1^1S_0 || Q_1 || 2^1P_1 \rangle \langle 1^1S_0 || Q_1 || 2^3P_1 \rangle \right. \\ \left. + \frac{4}{9} k_1^3 \langle 2^3S_1 || Q_1 || 2^1P_1 \rangle \langle 2^3S_1 || Q_1 || 2^3P_1 \rangle \right\}$$

⁴F. Robicheaux, T.W. Gorczyca, M.S. Pindzola, and N.R. Badnell, Phys. Rev. A **52**, 1319 (1995).

Complex Hyperfine Matrix – ^{107}Ag

\Re Energy Matrix in cm^{-1}

J=0	J=1	J=2	J'=1
0.0000[0]	-9.8681[1]	0.0000[0]	7.1835[0]
-9.8681[1]	-6.3399[3]	0.0000[0]	-1.2235[1]
0.0000[0]	0.0000[0]	1.6955[6]	0.0000[0]
7.1835[0]	-1.2235[1]	0.0000[0]	1.9426[6]

\Im Energy Matrix in cm^{-1}

3.0711[-3]	0.0000[0]	0.0000[0]	0.0000[0]
0.0000[0]	4.1967[3]	0.0000[0]	-6.5800[3]
0.0000[0]	0.0000[0]	2.0908[0]	0.0000[0]
0.0000[0]	-6.5800[3]	0.0000[0]	1.0317[4]

\Re Eigenvalues in cm^{-1}

1.0699[0]	-6.3188[3]	1.6955[6]	1.9426[6]
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$2\Im$ Eigenvalues in ns^{-1}

2.6851[2]	1.5807[6]	7.8768[2]	3.8868[6]
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$$A_{\text{rd}} = 268.5 \text{ ns}^{-1}$$

$$A_{\text{Expt}} = 251 \pm 23 \text{ ns}^{-1}$$

Comments

- ◇ For $Z < 40$, coherence of 2^3P_1 and 2^1P_1 contributions is important and perturbation theory works well.
- ♠ For $Z > 40$, coherence is unimportant but perturbation theory does not work.
- ♡ Radiation-damping theory works in both regions.

Two-Photon Decays

Electric dipole decays of 2^3S_1 and 2^1S_0 levels to the ground state are forbidden, leading to very long lifetimes for those states (about 20 ms for the He singlet).

- 2^1S_0 Angular momentum conservation forbids both $E1$ and $M1$ single photon decays of the 2^1S_0 state. Thus, the lifetime of the 2^1S_0 state is determined by **two-photon** transitions.
- 2^3S_1 $M1$ transitions are allowed for the 2^3S_1 states. The $M1$ rate is about 10^4 times larger than the two-photon rate for all $Z = 2 - 100$. Thus, the lifetime of the 2^3S_1 state is determined by **$M1$** transitions.

Historical Comment

- ★ The first theoretical two-photon decay rate for the 2^1S_0 state for helium was given by Dalgarno⁵.

- ★ 14 years ago, Drake⁶ gave highly accurate nonrelativistic values of two-photon decay rates of 2^1S_0 states for heliumlike ions with nuclear charges Z from 2 to 92, and estimated relativistic corrections to these rates.

- ★ Calculations of two-photon decay rates for 2^3S_1 states of He were made by Bely, Bely and Faucher, Drake and Dalgarno, and Drake, Victor, and Dalgarno.

⁵A. Dalgarno, Mon. Not. R. Astron. Soc. **131**, 311 (1966).

⁶G.W.F. Drake, Phys. Rev. A **34**, 2871 (1986).

Two-Photon Transition

The probability per unit time for a transition from state Ψ_I to state Ψ_F with the emission of two $E1$ photons, ω_1 and ω_2 , is

$$dw_{FI} = \frac{8}{9\pi} \alpha^6 \omega_1^3 \omega_2^3 d\omega_1 \sum_{M_1 M_2} |M_{M_2 M_1}|^2$$

$$M_{M_2 M_1} = - \sum_n \left[\frac{\langle \Psi_I | \mathcal{Q}_{M_2}(\omega_2) | \Psi_n \rangle \langle \Psi_n | \mathcal{Q}_{M_1}(\omega_1) | \Psi_F \rangle}{E_n + \omega_2 - E_I} + \frac{\langle \Psi_I | \mathcal{Q}_{M_1}(\omega_1) | \Psi_n \rangle \langle \Psi_n | \mathcal{Q}_{M_2}(\omega_2) | \Psi_F \rangle}{E_n + \omega_1 - E_I} \right]$$

CI Version of Dalgarno-Lewis Method

$$|\delta\Psi_{DM_1}\rangle = \sum_n \frac{|\Psi_n\rangle\langle\Psi_n|Q_{M_1}(k_1)|\Psi_F\rangle}{E_n + \omega_2 - E_I}$$

$$|\delta\Psi_{EM_2}\rangle = \sum_n \frac{|\Psi_n\rangle\langle\Psi_n|Q_{M_2}(k_2)|\Psi_F\rangle}{E_n + \omega_1 - E_I}.$$

$$(H + \omega_2 - E_I)|\delta\Psi_{DM_1}\rangle = Q_{M_1}(k_1)|\Psi_F\rangle$$

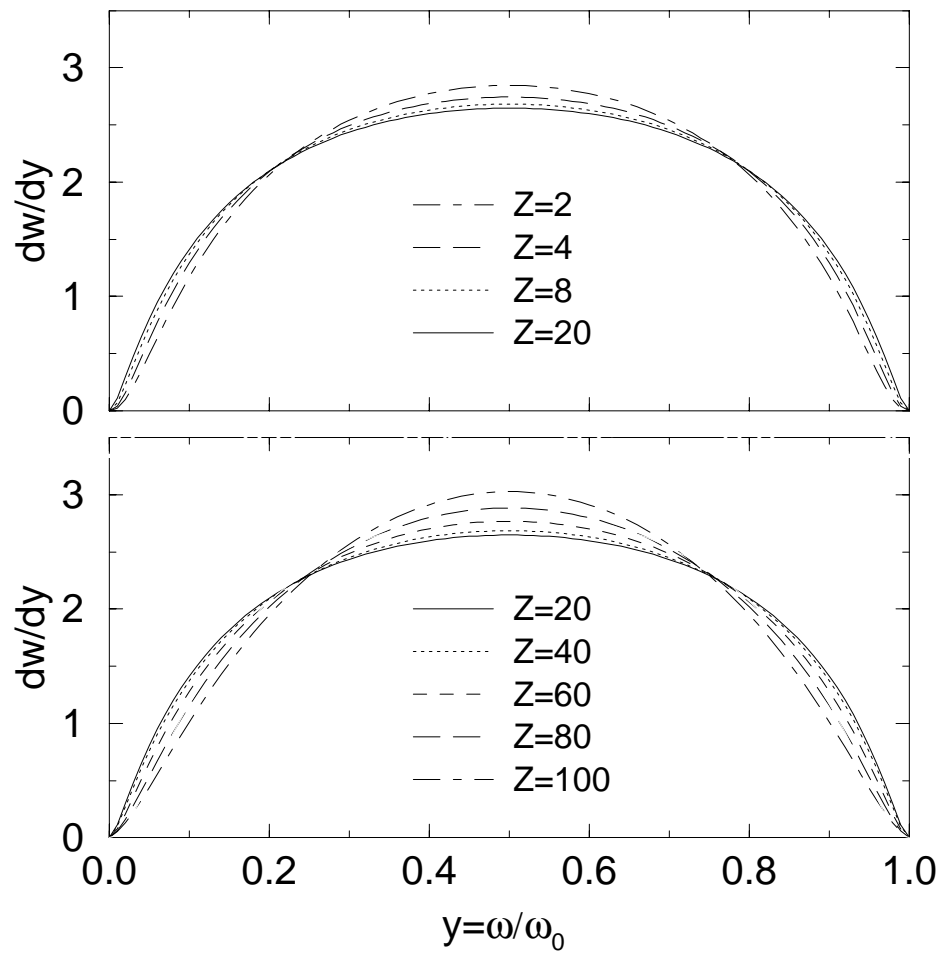
$$(H + \omega_1 - E_I)|\delta\Psi_{EM_2}\rangle = Q_{M_2}(k_2)|\Psi_F\rangle.$$

$$M_{M_2M_1} = D_{M_2M_1} + E_{M_2M_1}$$

$$D_{M_2M_1} = -\langle\Psi_I|Q_{M_2}(k_2)|\delta\Psi_{DM_1}\rangle$$

$$E_{M_2M_1} = -\langle\Psi_I|Q_{M_1}(k_1)|\delta\Psi_{EM_2}\rangle.$$

Energy Spectra



Theory vs. Experiment

2^1S_0 lifetimes for He-like ions

Z	$\tau_{th.}$	$\tau_{expt.}$	Ref.
2	1.962×10^{-2}	$1.97(0.10) \times 10^{-2}$	[a]
3	5.157×10^{-4}	$5.03(0.26) \times 10^{-4}$	[b]
18	2.364×10^{-9}	$2.30(0.30) \times 10^{-9}$	[c]
28	1.535×10^{-10}	$1.561(0.016) \times 10^{-10}$	[d]
35	3.938×10^{-11}	$3.932(0.032) \times 10^{-11}$	[e]
36	3.320×10^{-11}	$3.408(0.034) \times 10^{-11}$	[f]
41	1.514×10^{-11}	$1.533(0.060) \times 10^{-11}$	[g]

- a R.S. vanDyck, Jr., C.E. Johnson, and H.S. Shugart, Phys. Rev. **A4**, 1327 (1971).
- b M.H. Prior and H.A. Shugart, Phys. Rev. Lett. **27**, 902 (1971).
- c R. Marrus and R.W. Schmieder, Phys. Rev. **A5**, 1160 (1972).
- d R.W. Dunford, H.G. Berry, D.A. Church, M. Hass, C.J. Liu, M.L.A. Raphaelian, B.J. Zabransky, L.J. Curtis, and A.E. Livingston Phys. Rev. **A48**, 2729 (1993).
- e R.W. Dunford, H.G. Berry, S. Cheng, E.P. Kanter, C. Kurtz, B.J. Zabransky, A.E. Livingston, and L.J. Curtis, Phys. Rev. **A48**, 1929 (1993).
- f R. Marrus, V.S. Vicente, P. Charles, J.P. Briand, F. Bosch, D. Liesen, and I. Varga, Phys. Rev. Lett. **56**, 1683 (1986).
- g A. Simionovici, B.B. Birkett, J.P. Briand, P. Charles, D.D. Dietrich, K. Finlayson, P. Indelicato, D. Liesen, and R. Marrus, Phys. Rev. **A48**, 1695 (1993).

Polarizabilities

Motivation: Theoretical⁷ and experimental⁸ energy intervals in high Rydberg states of ⁷Li differ by a small amount that can be understood as a relativistic correction to the polarizability of the Li⁺ core!

Energy intervals in MHz

Interval	Theory [7]	Expt. [8]
10G-10H	339.80±0.11	339.7186±0.0031
10H-10I	109.2466±0.0011	109.2140±0.0047
10I-10K	42.7958±0.0003	

ΔE_{rel} from a relativistic CI calculation of α_d

10G-10H	-0.0782±0.0009
10H-10I	-0.0245±0.0001

⁷R. J. Drachman and A. K. Bhatia, Phys. Rev. **51**, 2926 (1995).

⁸N. E. Rothery, C. H. Storry, and E. A. Hessels, Phys. Rev. A **51**, 2919 (1995).

Method

$$\alpha_d = 2 \sum_n \frac{\langle \Psi_0 | \mathcal{Z} | \Psi_n \rangle \langle \Psi_n | \mathcal{Z} | \Psi_0 \rangle}{E_n - E_0}$$

$$\alpha = -2 \langle \Psi | \mathcal{Z} | \Psi_0 \rangle$$

$$(H - E_0) | \Psi \rangle = -\mathcal{Z} | \Psi_0 \rangle$$

Nonrelativistic CI Calculation

Partial wave contributions to the polarizability α_l and electric-dipole shielding factor σ_l of heliumlike neon ($Z = 10$). Units of α : m.a.u.

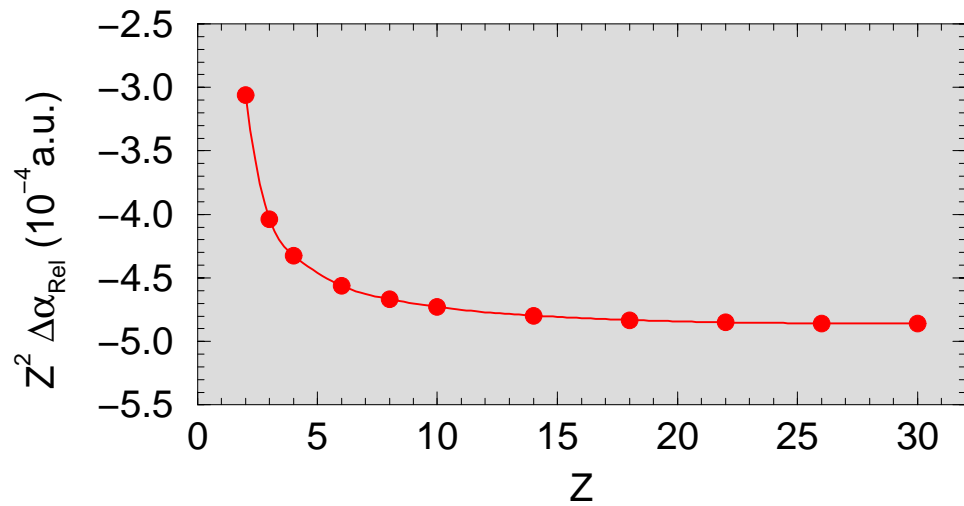
Ψ_0	Ψ	α_l	$\alpha_l - \alpha_{l-1}$	σ_l	$\sigma_l - \sigma_{l-1}$
(s, s)	(s, p)	1.0564619		0.2037619	
(p, p)	(p, d)	1.0446033	-0.0118586	0.1999394	-0.0038225
(d, d)	(d, f)	1.0447408	0.0001375	0.1999824	0.0000430
(f, f)	(f, g)	1.0447696	0.0000288	0.1999923	0.0000099
(g, g)	(g, h)	1.0447799	0.0000103	0.1999959	0.0000036
(h, h)	(h, i)	1.0447845	0.0000046	0.1999976	0.0000016
Limit	$(\ell \geq 6)$	1.0447909	0.0000064	0.1999998	0.0000023

Rel. - Non Rel. Calculation

Differences between partial wave contributions to relativistic and nonrelativistic polarizabilities for heliumlike neon ($Z = 10$). Units: m.a.u.

ℓ	α_{NR}	α_{Coul}	$\Delta\alpha_{\text{Coul}}$	α_{Rel}	$\Delta\alpha_{\text{Rel}}$
0	1.056462	1.051281	-0.005181	1.051805	-0.004657
1	1.044603	1.039503	-0.005100	1.039879	-0.004724
2	1.044741	1.039640	-0.005101	1.040014	-0.004727
3	1.044770	1.039668	-0.005101	1.040042	-0.004728
4	1.044780	1.039679	-0.005101	1.040051	-0.004729

$$\Delta\alpha_{\text{Rel}}$$



Large Z :
$$\Delta\alpha_{\text{Rel}} \rightarrow -\frac{4.86 \times 10^{-4}}{Z^2} \text{ (a.u.)}$$

Summary

- ★ Relativistic CI calculations give accurate energies and wave functions for two electron ions.
- ★ Transition amplitudes calculated using CI wave functions differ in L and V forms because of omitted negative-energy contributions. The missing contributions can be estimated using perturbation theory.
- ★ The hyperfine interaction matrix can be accurately evaluated using CI wave functions. Radiation damping methods are useful near zeros of the fine-structure intervals.
- ★ Two-photon rates can be accurately evaluated using CI wave functions. An operator version of the Dalgarno-Lewis method is useful for this purpose.
- ★ Relativistic corrections to polarizabilities can be evaluated by comparing relativistic and nonrelativistic CI calculations.