Relativistic CI Studies for Heliumlike Ions

W.R. Johnson
Notre Dame University
http://www.nd.edu/∼johnson

Abstract

Relativistic CI calculations of energies and wave functions for heliumlike ions starting from the $no\text{-}pair$ 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

- K.T. Cheng and Mau Chen (LLNL)
- J. Sapirstein (ND)
- D. Plante (Stetson)
- A. Derevianko (ITAMP)

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* Hamiltonian[1] (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.

[1] Brown, G.E. & Ravenhall, D.G. 1951 *Proc. R. Soc. London,* Ser. A **208**, 552-559.

CI for He-like Ions – How?

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

$$\Phi_{ij}(JM) = \eta_{ij}\sum_{m_i m_j} \langle j_i m_i j_j m_j | JM\rangle\, a^\dagger_{im_i} a^\dagger_{jm_j}|0\rangle$$

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

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

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

Example: $^3\mathrm{P}_0^o$ States

Parity: $l_i + l_j$ odd
Angular Momentum: $|j_i - j_j| \le 0$
$\Rightarrow \kappa_i = -\kappa_j$

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 $l \le 6$ 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 routine[2] to solve the eigenvalue problem.

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

Convergence Pattern for $2\,^3\mathrm{P}_0$

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:

$2\,^3\mathrm{P}_0 - 2\,^3\mathrm{S}_1$ 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

($\dagger$) $2\,^3\mathrm{P}_2 - 2\,^3\mathrm{S}_1$

($*$) $2\,^3\mathrm{P}_2 - 1\,^1\mathrm{S}_0$

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.

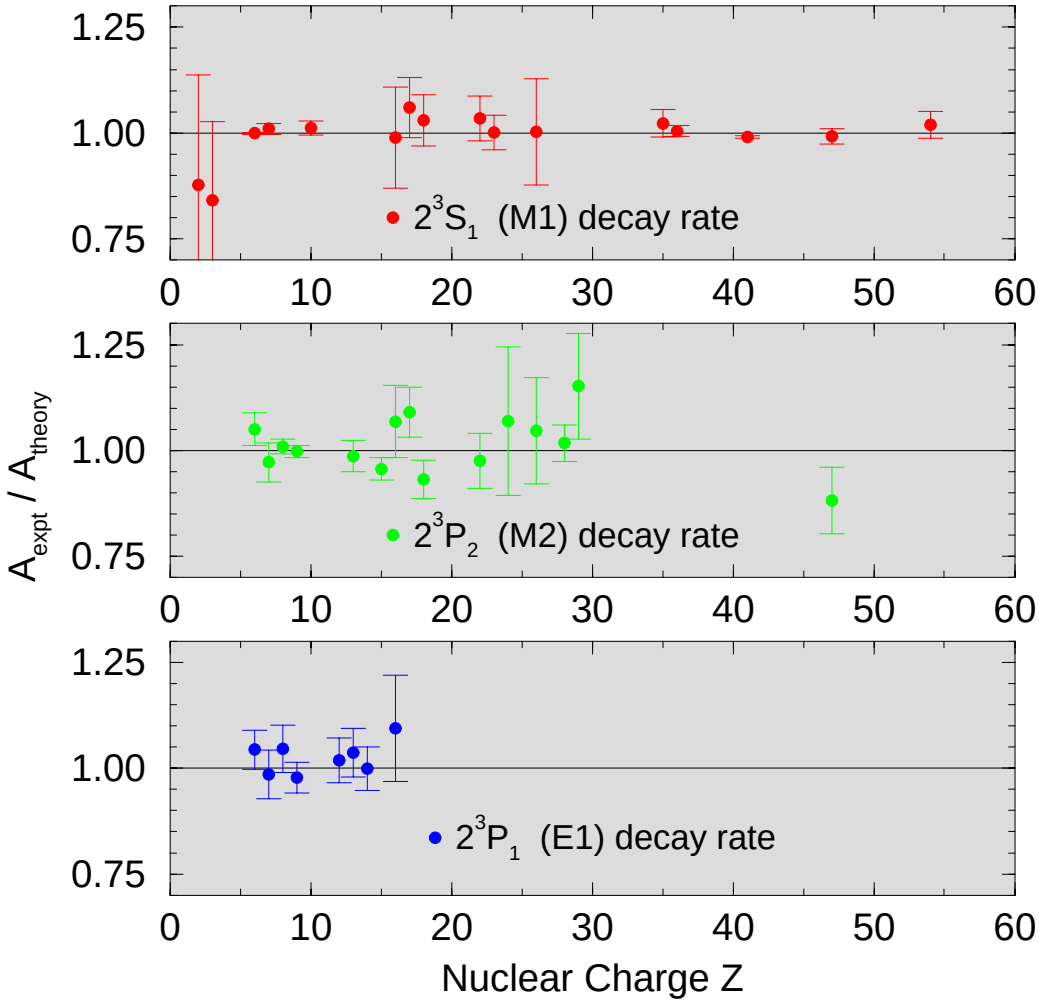
Patch from QED

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

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

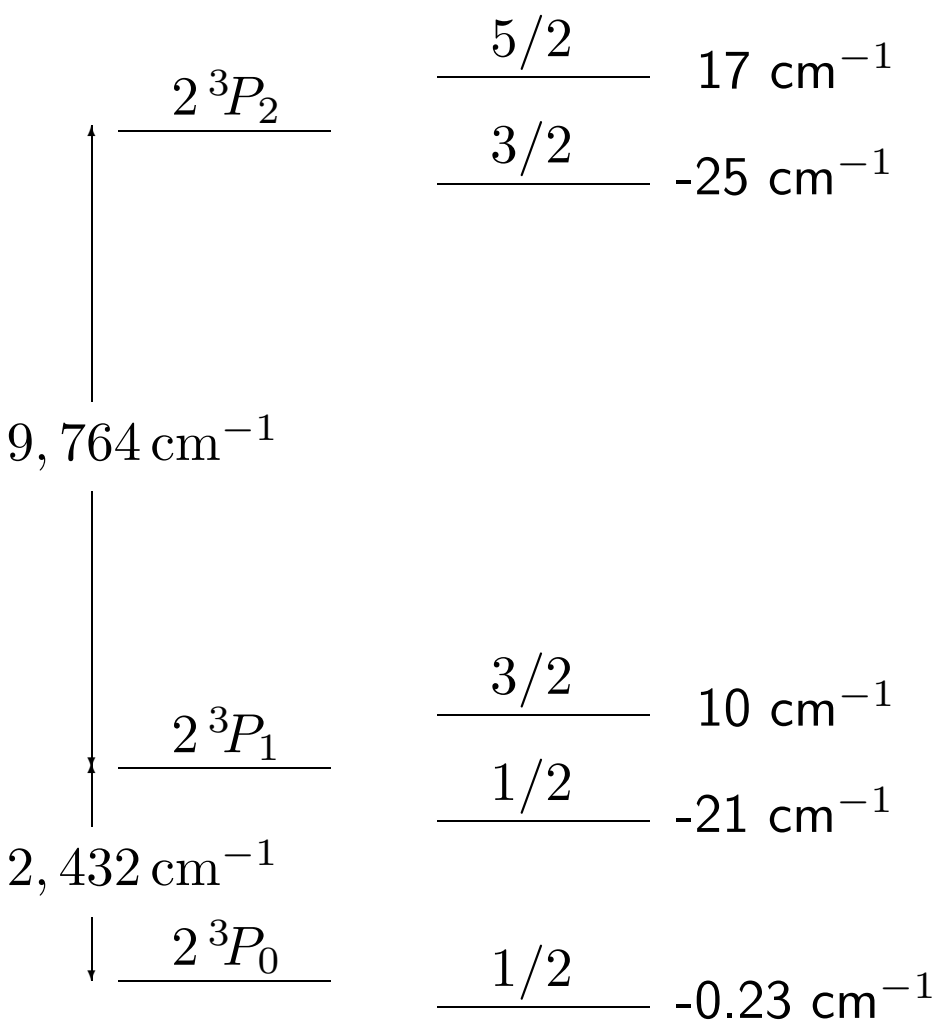
Type	$\langle F\|\|Q_1\|\|I\rangle^{(+)}$	$\langle F\|\|Q_1\|\|I\rangle^{(-)}$	$\Delta Q(l-v)$
CI(l)	0.057636		
CI(v)	0.057345		0.000291
QED(l)	0.057668	-7×10^{-8}	
QED(v)	0.057373	0.000295	0.000000
CI+QED(l)	0.057636	-7×10^{-8}	
CI+QED(v)	0.057345	0.000295	-0.000004

Measured Transition Rates



Hyperfine Structure

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



HFS Theory

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

$$|FM_F\rangle = \sum_{\gamma J} C^F_{\gamma J} \, \langle IM_I, JM_J | FM_F\rangle \, |IM_I\rangle |\gamma J M_J\rangle$$

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

$$W_F C^F_{\gamma J} = \sum_{\gamma' J'} W^F_{\gamma J, \gamma' J'} \, C^F_{\gamma' J'}$$

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

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

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 $^{31}P^{13+}$

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

	J	F	cm^{-1}
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

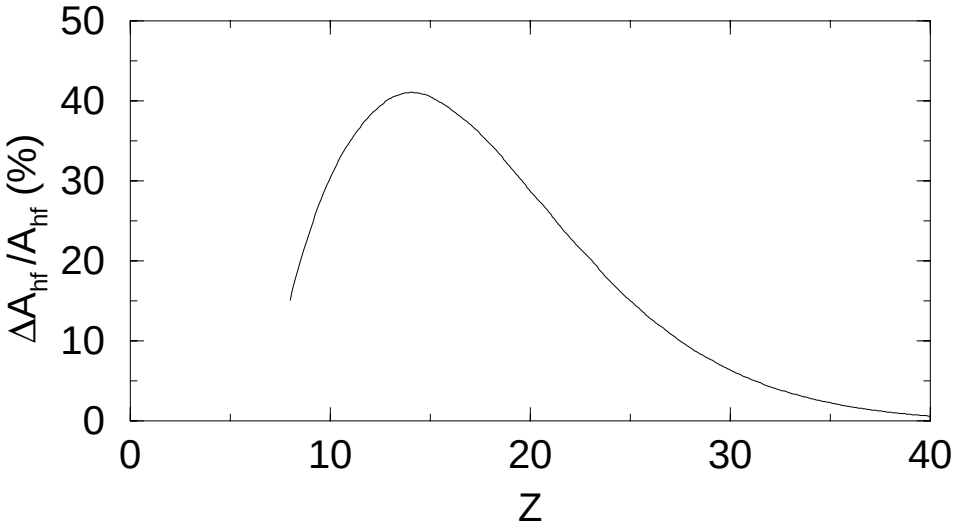
Quenching & Coherence

Dipole transitions from $2\,^3P_J$ state to ground state

$$A_{E1} = \frac{2.02613 \times 10^{18}}{\lambda^3} \times$$

$$\sum_F \frac{[F]}{3[I][J]} \left| \sum_{\gamma=1,3} C^F_{\gamma 1} \langle 1\,^1S_0 \| Q_1 \| 2\,^\gamma P_1 \rangle \right|^2$$

Importance of including $2\,^1P_1$ states:

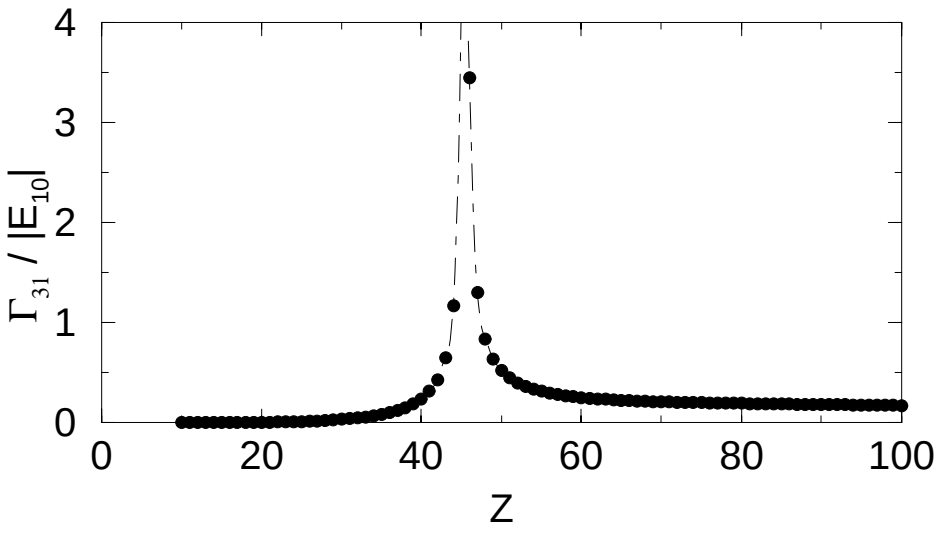


Results

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

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):

$A_{\rm Pert} = 384.8$ ns^{-1}
$A_{\rm Expt} = 251 \pm 23$ ns^{-1}

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

Radiation Damping[4]

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

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

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

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

[4] F. 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]

$2\Im$ Eigenvalues in ns^{-1}

2.6851[2]	1.5807[6]	7.8768[2]	3.8868[6]

$A_{\rm rd} = 268.5$ ns^{-1}

$A_{\rm Expt} = 251 \pm 23$ 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 Dalgarno[5].

- 14 years ago, Drake[6] 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.

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

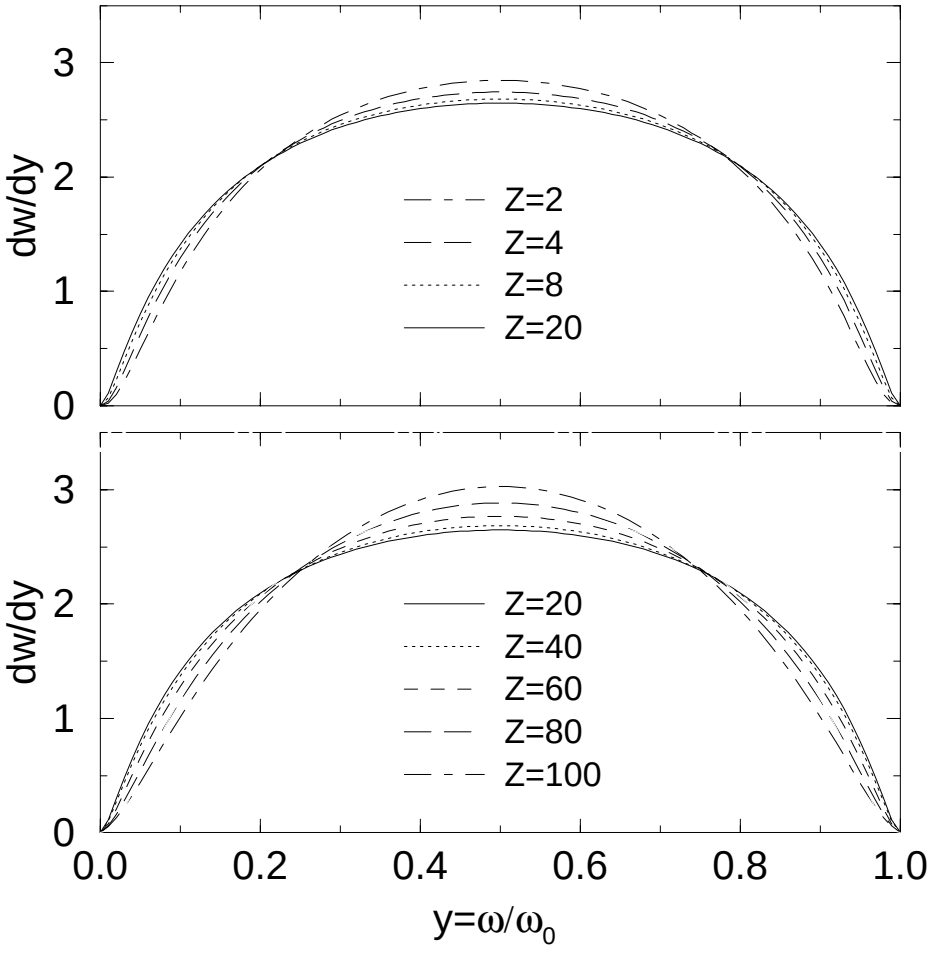
$$\begin{aligned}
\left|\delta\Psi_{DM_1}\right\rangle &= \sum_n \frac{|\Psi_n\rangle\langle\Psi_n|Q_{M_1}(k_1)|\Psi_F\rangle}{E_n+\omega_2-E_I} \\
\left|\delta\Psi_{EM_2}\right\rangle &= \sum_n \frac{|\Psi_n\rangle\langle\Psi_n|Q_{M_2}(k_2)|\Psi_F\rangle}{E_n+\omega_1-E_I}\,.
\end{aligned}$$

$$\begin{aligned}
(H+\omega_2-E_I)|\delta\Psi_{DM_1}\rangle &= Q_{M_1}(k_1)|\Psi_F\rangle \\
(H+\omega_1-E_I)|\delta\Psi_{EM_2}\rangle &= Q_{M_2}(k_2)|\Psi_F\rangle\,.
\end{aligned}$$

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

$$\begin{aligned}
D_{M_2M_1} &= -\langle\Psi_I|Q_{M_2}(k_2)|\delta\Psi_{DM_1}\rangle \\
E_{M_2M_1} &= -\langle\Psi_I|Q_{M_1}(k_1)|\delta\Psi_{EM_2}\rangle\,.
\end{aligned}$$

Energy Spectra



Theory vs. Experiment

$2\,^1S_0$ lifetimes for He-like ions

Z	$\tau_{th.}$	$\tau_{\rm expt.}$	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. A**4**, 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. A**5**, 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. A**48**, 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. A**48**, 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. A**48**, 1695 (1993).

Polarizabilities

Motivation: Theoretical[7] and experimental[8] energy intervals in high Rydberg states of ^{7}Li 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	

$\Delta E_{\rm rel}$ from a relativistic CI calculation of $\alpha_{\rm d}$

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

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

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

Method

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

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

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

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.

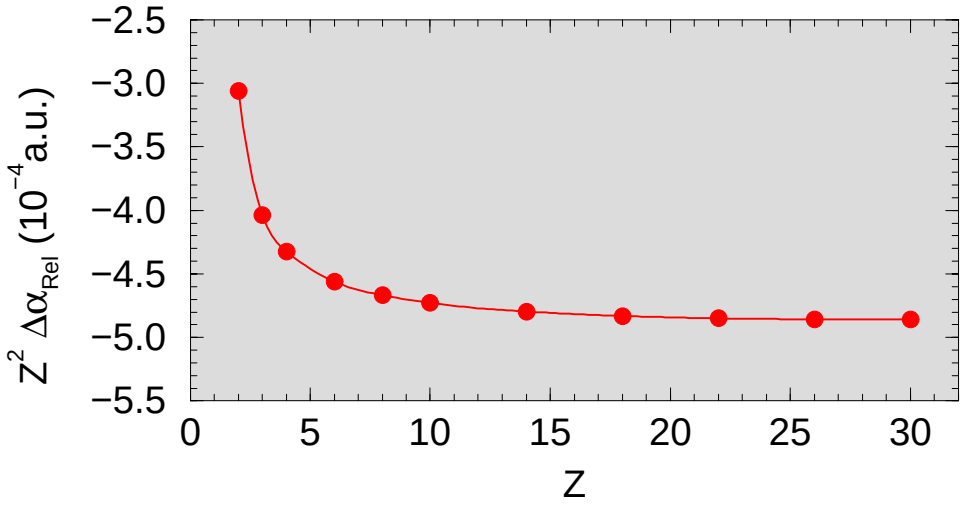
Ψ_0	Ψ	α_l	$\alpha_\ell - \alpha_{\ell-1}$	σ_l	$\sigma_\ell - \sigma_{\ell-1}$
(s,s)	(s,p)	1.0564619		0.2037619	
(p,p)	(p,d)	1.0446033	-0.0118586	0.1999394	-0.0038225
(d,d)	(d,f)	1.0447408	0.0001375	0.1999824	0.0000430
(f,f)	(f,g)	1.0447696	0.0000288	0.1999923	0.0000099
(g,g)	(g,h)	1.0447799	0.0000103	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	$\alpha_{\rm NR}$	$\alpha_{\rm Coul}$	$\Delta\alpha_{\rm Coul}$	$\alpha_{\rm Rel}$	$\Delta\alpha_{\rm Rel}$
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

$\Delta\alpha_{\rm Rel}$



Large Z: $\qquad \Delta\alpha_{\rm Rel} \to -\dfrac{4.86\times10^{-4}}{Z^2}\ ({\rm a.u.})$

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.