

Breit–Pauli and Dirac–Hartree–Fock energy levels and transition probabilities in neutral argon

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Abstract

Breit–Pauli and Dirac–Hartree–Fock energy levels and transition probabilities in Ar I are reported for energy levels up to and including $3s^23p^53d^1P_1^o$. Through the use of a simple core-polarization model, the term composition of these levels was determined. In order to also obtain accurate results for transitions from the ground state, a more extended correlation model was employed. The agreement in the length and velocity gauges of transition data and the accuracy of the predicted transition energy are factors that determine the accuracy of our results which are compared with experimental and other theoretical data when available.

1. Introduction

Energy levels and transition probabilities of neutral argon are useful in a variety of scientific applications. Argon has been employed successfully to determine reactive species concentrations using optical emission spectroscopy of discharge plasmas [1, 2]. The Ar I spectrum was also used in an astrophysical study concerning the abundance of elements in a damped Lyman α system, where the presence of this neutral atom was used to derive metal abundances consistent with the theory of nucleosynthesis [3]. In research undertaken with the goal of determining column densities in another damped Lyman α system [4], the absorption spectrum of neutral argon was found useful. This type of system had been found to greatly contribute to the neutral gas mass in the early ages of the Universe and the low depletion factor of argon in the interstellar medium studied was beneficial in this second study of its kind that measured argon at high redshift [4].

Among the experimental methods that have been used to study oscillator strengths for $3p^6 \rightarrow 3p^54s$ transitions in neutral argon are line-broadening by Copley and Camm [5] and Vallee *et al* [6], as well as self-absorption by Westerveld *et al* [7]. Electron–photon delayed coincidence was used, among others, by Chornay *et al* [8] to measure radiative lifetimes of

$3p^54s$ excited states. A study of oscillator strengths for two $3p^6 \rightarrow 3p^54s$ transitions was performed in 1992 by Federman *et al* using an experimental beam-foil method [9]. In 1995, Wu *et al* [10] employed an electron energy-loss spectrometer to determine absolute oscillator strengths for a number of transitions, including $3p^6 \rightarrow 3p^53d, 4s$ and $5s$. Ligtenberg *et al* [11] and Gibson and Risley [12], in turn, reported absolute measurements of optical oscillator strengths for resonance lines in noble gases, including argon. In a recent study by Savukov and Berry [13], the ratio of line strengths for the two transitions $3p^54s \ ^1P_1^o \rightarrow 3p^54p \ ^3P_2$ and $3p^54s \ ^1P_1^o \rightarrow 3p^54p \ ^3D_2$ was measured in an argon pulse discharge using a single-mode Ti:sapphire laser.

Early theoretical studies of oscillator strengths [14, 15–17] include an atomic eigenchannel calculation of excitation energies and oscillator strengths for several high-lying configurations undertaken by Lee in 1974 [17]. Oscillator strengths for E1 transitions in the Ar-like sequence from the ground state to $3p^5nd$ ($n = 3, 4$) and $4s$ were investigated by Lin *et al* in two ways, namely with the multiconfiguration Hartree–Fock (MCHF) and Dirac–Hartree–Fock (DHF) methods [18]. In this study, however, orbital expansions were limited. In 1997, a particle–hole model was used by Avgoustoglou and Beck [19] to compute oscillator strengths in $np^6 \rightarrow np^5(n+1)s$ dipole transitions for several rare gases including argon with results that agreed reasonably well with both experiment and other theory. More recently, theoretical energies and transition probabilities were computed by Savukov using a combined configuration interaction and many-body-perturbation-theory approach [20].

Although accurate transition data in neutral argon is important not only in astronomy and astrophysics but also in other scientific areas such as plasma physics, there are unfortunately few investigations of Ar I beyond the resonance lines. Many of the investigations performed in the past were restricted to transitions from the ground state to the excited states $3p^54s$, $3p^54p$ and $3p^53d$, while transitions between excited states have not been studied by many authors. In this paper, we report and discuss the results of our calculation of energy levels, transition probabilities, line and oscillator strengths for neutral argon states up to and including $3p^53d \ ^1P_1^o$, particularly for transitions between excited states. This study is part of a larger undertaking to compute all the energy levels in a lower portion of an atomic spectrum for a number of isoelectronic sequences. Our large-scale investigation is motivated by the need for accurate transition data in a variety of scientific applications. As a result of computing atomic transitions, lifetimes can also be presented, which offer another way of comparing our results with experiment and other theory.

2. Computational methods

The theoretical basis of our computational approach has been widely discussed elsewhere [21–23]. Two computational procedures were used, namely the MCHF with Breit–Pauli relativistic corrections and the multiconfiguration Dirac–Hartree–Fock (MCDHF) method.

In both procedures, calculations were performed using an expansion of configuration state functions (CSFs) derived from an orbital set. To build a CSF expansion, the restrictive active space method was used to generate CSFs by excitation of orbitals occurring in the reference set of configurations to a set of orbitals, where an inactive $1s^22s^22p^6$ common core was assumed. In general, the correlation model employed determines how this is done. The orbital set was increased systematically in order to monitor the convergence of the calculation. It is convenient to refer to the $\{1s, 2s, 2p, \dots, 3s, 3p, 3d\}$ set of orbitals as the $n = 3$ orbital set, $\{1s, 2s, 2p, \dots, 4s, 4p, 4d, 4f\}$ as $n = 4$, etc. Larger orbital sets can result in a considerable increase of computational time required for the problem, and appropriate restrictions may be necessary.

In the MCHF approach, orbitals are determined by optimization of an energy expression for an LS term. Since these orbitals will be ultimately used in a Breit–Pauli configuration interaction (CI) calculation involving many LS terms, the MCHF method has been extended to optimize on a weighted linear combination of energy expressions thereby optimizing orbitals simultaneously for a group of terms. Radial functions and expansion coefficients were optimized to self-consistency using the multiconfiguration self-consistent field (MC-SCF) procedure [24]. The iterative Davidson method [25] was used to determine the desired eigenvalues and eigenvectors. In this manner, an approximate wavefunction Ψ was determined for each term γLS of the form

$$\Psi(\gamma LS) = \sum_j c_j \Phi(\gamma_j LS) \quad (1)$$

where γ usually represents the dominant configuration and any additional quantum numbers necessary to specify the state uniquely. The configuration state functions (CSFs) were built from a basis of one-electron spin orbitals,

$$\phi_{nlm_l m_s} = \frac{1}{r} P_{nl}(r) Y_{lm_l}(\theta, \phi) \chi_{m_s}, \quad (2)$$

where the radial functions $P_n(r)$ were determined by the SCF process.

The above expansions and orbitals were then used in a configuration interaction (CI) calculation where the interaction matrix was a Breit–Pauli interaction matrix [24]. All contributors to the Breit–Pauli Hamiltonian were included in the calculation presented here with the exception of the orbit–orbit interaction term, which does not contribute to interactions between CSFs from different LS terms. The eigenfunctions of the Breit–Pauli interaction matrix are the intermediate coupling wavefunctions

$$\Psi(\gamma J) = \sum_{LS} \sum_j c_j(LSJ) \Phi(\gamma_j LSJ) \quad (3)$$

where γ represents the configuration and any other quantum numbers required to specify a state. The expansion coefficients, $c_j(LSJ)$, and the corresponding energy, $E(LSJ)$, are an eigenvector and eigenvalue, respectively, of the interaction matrix. It is convenient to think of the Breit–Pauli interaction matrix as having a block structure, where the diagonal blocks are the interactions within an LS term, and off-diagonal blocks represent the interaction between terms. We refer to two LS terms as interacting if, for some value of J , there are non-zero interactions in the off-diagonal block for the pair of LS terms.

In the MCDHF procedure, the wavefunction Ψ for the state labelled γJ is approximated by an expansion over jj -coupled CSFs

$$\Psi(\gamma J) = \sum_j c_j \Phi(\gamma_j J), \quad (4)$$

where the CSF $\Phi(\gamma J)$ are antisymmetrized linear combinations of relativistic orbital products of the form

$$\phi(\mathbf{r}) = \frac{1}{r} \begin{pmatrix} P_{n\kappa}(r) \chi_{\kappa m}(\hat{r}) \\ i Q_{n\kappa}(r) \chi_{-\kappa m}(\hat{r}) \end{pmatrix}. \quad (5)$$

Here κ is the relativistic angular momentum, $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$ are the large and small component radial wavefunctions and $\chi_{\kappa m}(\hat{r})$ is the spinor spherical harmonic in the lsj coupling scheme [22]. After obtaining the set of radial functions, relativistic configuration interaction calculations were carried out to determine CSF expansion coefficients by diagonalizing the Hamiltonian matrix that included the frequency-dependent Breit interaction, vacuum polarization and self-energy correction.

Table 1. Selected non-relativistic line strengths obtained from the MCHF core-polarization model. Per cent differences were computed according to the formula $[S(l) - S(v)] \times 100 / \max\{S(l), S(v)\}$.

n	$S(l)$	$S(v)$	Difference (%)	n	$S(l)$	$S(v)$	Difference (%)
$3p^6\ ^1S - 3p^54s\ ^1P^o$				$3p^54s\ ^3P^o - 3p^54p\ ^3D$			
4	1.627	1.779	-8	4	149.8	164.6	-8
5	1.007	0.714	29	5	138.2	128.8	6
6	0.973	0.640	34	6	133.8	136.3	-1
7	0.976	0.638	34	7	133.5	133.5	0
8	0.967	0.635	34	8	130.0	135.3	-3
$3p^6\ ^1S - 3p^53d\ ^1P^o$				$3p^54p\ ^3P - 3p^53d\ ^3D^o$			
4	3.323	1.067	67	4	249.0	293.5	15
5	0.651	0.328	49	5	230.3	257.3	-10
6	0.459	0.287	37	6	227.0	230.0	-1
7	0.396	0.281	29	7	227.0	232.0	-2
8	0.431	0.278	35	8	228.4	229.6	-1

3. Core-polarization model

Many transitions of interest in Ar I are between excited states where few data are available. Since the only parent for an outer electron in this atom is $3p^5\ ^2P$, a simple core-polarization model was implemented first. In this approach, the wavefunction is an expansion over odd or even $3s^23p^4nl\ n'l'$ and $3s3p^5nl\ n'l'$ configuration states, where nl and $n'l'$ are orbitals from the orbital set. Since the expansions for the terms are not too long in this model, one set of orbitals could be optimized for all the even terms and another for all the odd terms. This model had proved to be very effective for computing $2p^4(^3P)3p - 2p^4(^3P)3d$ transitions in Ne II [22].

In Ar I, only configurations with $l \leq g$ were included in the expansions and only orbitals outside the core were varied in calculations which were performed for $3 \leq n \leq 7$. At the $n = 8$ level, only $8s$ and $8p$ orbitals were added.

As a measure of convergence and accuracy of our calculation, we monitored the length and velocity forms of the MCHF line strength for orbital sets of increasing size, denoted by n . In table 1 we present four selected transitions, two from the ground state and two between excited states. As can be seen from this table, the agreement of the two gauges is better for transitions between excited states than it is for those involving the ground state. These examples illustrate the fact that the core-polarization model is not able to accurately compute the relative energy differences between the ground and excited states. In the case of transitions between excited states, however, the agreement of the two gauges improves with increasing n .

To check the reliability of our core-polarization results, a similar calculation was performed using the MCDHF method. Expansions were generated in the same fashion as in the Breit–Pauli model, but only up to $n = 6$ and $l \leq g$. For odd states, $7s$ and $7d$ orbitals were also included.

Table 2 displays the energy levels computed using our two *ab initio* models—MCDHF and Breit–Pauli—as well as differences from experimental values specified in the NIST atomic spectra database [26]. Both MCDHF and Breit–Pauli energies are shifted upwards significantly due to the fact that the core-polarization expansion applied to the ground state includes correlation among the equivalent $3p$ electrons, correlation omitted in the excited states. This shift is greater for Breit–Pauli than MCDHF. Thus transition energies for transitions from the ground state are in error by up to 25% for MCDHF. However, by considering both present and NIST energy levels relative to $3p^54s\ ^3P^o_2$ the differences are much smaller. For MCDHF

Table 2. Ar *ab initio* energies, energy differences (computed – observed [26]) in cm^{-1} , and term compositions for states up to and including $3p^53d^1P_1^o$ from core-polarization calculations.

Term	MCDHF		Breit–Pauli		Term composition (%)
	Level	Difference	Level	Difference	
$3p^6$					
1S_0	0.00	0.00	0.00	0.00	100 1S_1
$3p^54s$					
$^3P_2^o$	124797.16	31653.40	125732.17	32588.41	100 $^3P_2^o$
$^3P_1^o$	125403.69	31653.09	126320.54	32569.94	83 $^3P_1^o$ 17 $^1P_1^o$
$^3P_0^o$	126177.09	31623.42	127036.75	32483.08	100 $^3P_0^o$
$^1P_1^o$	127055.98	31656.15	127937.44	32537.61	83 $^1P_1^o$ 17 $^3P_1^o$
$3p^54p$					
3S_1	136155.10	32053.00	136874.30	32772.20	96 3S_1 3 3P_1 1 1P_1
3D_3	137376.33	31913.57	138260.60	32797.84	100 3D_3
3D_2	137533.65	31916.38	138424.00	32806.73	65 3D_2 33 1D_2 2 3P_2
3D_1	137965.96	31878.70	138852.88	32765.62	53 3D_1 32 1P_1 15 3P_1
3P_2	138141.78	31904.23	139048.15	32810.60	55 3P_2 36 1D_2 9 3D_2
3P_0	138970.18	31915.91	139835.42	32781.15	85 3P_0 15 1S_0
3P_1	139354.12	31857.70	140204.50	32708.08	71 3P_1 25 1P_1 4 3S_1
1P_1	138984.97	31853.26	139822.03	32690.32	47 3D_1 42 1P_1 11 3P_1
1D_2	139171.76	31882.06	140009.91	32720.21	43 3P_2 31 1D_2 26 3D_2
1S_0	140868.80	32146.18	141517.71	32795.09	85 1S_0 15 3P_0
$3p^53d$					
$^3P_0^o$	142779.85	31112.08	143731.16	32063.39	100 $^3P_0^o$
$^3P_1^o$	142950.23	31132.20	143889.68	32071.65	99 $^3P_1^o$ 1 $^3D_1^o$
$^3P_2^o$	143309.48	31170.56	144224.45	32085.53	96 $^3P_2^o$ 2 $^3D_2^o$ 2 $^1D_2^o$
$^3F_4^o$	144417.93	31667.78	145375.82	32625.67	100 $^3F_4^o$
$^3F_3^o$	144702.08	31681.72	145655.97	32635.61	81 $^3F_3^o$ 16 $^1F_3^o$ 3 $^3D_3^o$
$^3F_2^o$	145101.91	31675.95	146041.80	32615.84	70 $^3F_2^o$ 19 $^1D_2^o$ 11 $^3D_2^o$
$^1F_3^o$	145471.06	31754.50	146426.64	32710.08	52 $^1F_3^o$ 44 $^3D_3^o$ 4 $^3F_3^o$
$3p^55s$					
$^1P_1^o$	145643.21	31999.95	146569.82	32926.56	55 $^1P_1^o$ 45 $^3P_1^o$
$^3P_2^o$	145455.32	31986.85	146384.48	32916.01	99 $^3P_2^o$ 1 $^3D_2^o$
$^3P_0^o$	146833.45	31971.81	147692.68	32831.04	100 $^3P_0^o$
$^3P_1^o$	146948.35	31973.33	147808.22	32833.20	54 $^3P_1^o$ 46 $^1P_1^o$
$3p^53d$					
$^1D_2^o$	146315.43	31674.44	147217.77	32576.78	59 $^1D_2^o$ 29 $^3F_2^o$ 12 $^3D_2^o$
$^3D_1^o$	146034.49	31886.76	146987.76	32840.03	70 $^3D_1^o$ 29 $^1P_1^o$ 1 $^3P_1^o$
$^3D_2^o$	146479.53	31674.39	147390.77	32585.63	74 $^3D_2^o$ 20 $^1D_2^o$ 4 $^3P_2^o$
$^3D_3^o$	146534.90	31712.96	147431.88	32609.94	53 $^3D_3^o$ 32 $^1F_3^o$ 15 $^3F_3^o$
$^1P_1^o$	147289.38	31922.51	148188.71	32821.84	70 $^1P_1^o$ 27 $^3D_1^o$ 3 $^3P_1^o$

the largest positive difference is 493 cm^{-1} for $3p^54p^1S_0$ for an error of 3% in the excitation energy whereas the largest negative difference is -543 cm^{-1} for $3p^53d^3P_0^o$. For Breit–Pauli, these differences are 206.9 cm^{-1} and -525 cm^{-1} , respectively. This suggests that the

Table 3. Compared relativistic line strengths in the Breit–Pauli and MCDHF core-polarization models. Per cent differences were computed according to the formula $[S(l) - S(v)] \times 100 / \max\{S(l), S(v)\}$.

	$S(l)$	$S(v)$	Difference (%)	$S(l)$	$S(v)$	Difference (%)
	$3p^6\ ^1S_0 - 3p^54s\ ^1P_1^o$			$3p^54s\ ^3P_2^o - 3p^54p\ ^3D_3$		
MCDHF	0.79	0.53	32	61.78	62.16	-1
Breit–Pauli	0.80	0.52	35	61.75	63.42	-3
	$3p^6\ ^1S_0 - 3p^53d\ ^1P_1^o$			$3p^54p\ ^3P_2 - 3p^53d\ ^3D_2^o$		
MCDHF	0.34	0.20	41	22.84	21.61	5
Breit–Pauli	0.35	0.21	40	22.42	22.47	0

core-polarization model is only appropriate for computing transition probabilities between excited states. At the same time, it indicates that the core-polarization model is a reasonable one for computing the term composition of levels in Ar I, which is presented in the last column of table 2.

The p^5l spectrum is an interesting one. At the Hartree-Fock level, the 1P and 3P terms of p^5p' are degenerate and, similarly, the $^1D^o$ and $^3D^o$ terms of p^5d are degenerate. In Ar I, all other terms are separated by about 400 cm^{-1} or more. Because the core-polarization effect is small, the non-relativistic LS term energies remain nearly degenerate when correlation is added and the relativistic corrections induce strong mixing of terms in certain levels.

Table 2 confirms the strong mixing of terms in 1P_1 and 3P_1 levels, on the one hand, and $^1D_2^o$ and $^3D_2^o$ levels, on the other hand. Two interesting examples are the $3p^54p\ ^1D_2$ and 1P_1 levels, where the leading terms are 3P_2 and 3D_1 , respectively. To correctly label the $3p^54p\ ^1D_2$ level, it was necessary to note that all the lower eigenvalues in $3p^54p$ with $J = 2$ had strong dominant compositions and could be labelled appropriately with certainty, leaving the third eigenvalue to be identified as 1D_2 by default. Similarly, the leading terms in the first three levels of $3p^54p$ with $J = 1$ were found to be 3P_1 , 3D_1 and 3P_1 , which pointed to the fact that the fourth level was 1P_1 , by elimination. (Note that the levels in table 2 are not ordered by energy.) In their study of the electron-impact ionization process in Ar I, Dasgupta *et al* [1] employed a method similar to the Hartree–Fock–Slater procedure but they used observed energies and adjusted some parameters for obtaining 4s and 4p orbitals. A CI calculation was then performed that included the spin–orbit interaction. Their mixing coefficients for states are in good agreement with ours for the $3p^54s$ levels and for $3p^54p$ their labels for energy levels agree with ours.

To ensure the consistency of this analysis, our term mixing results were also reproduced from the MCDHF wavefunction by a transformation from jj to LSJ coupling that confirmed our labelling. The $3p^53d\ ^1P_1^o$ and $^3P_1^o$ levels show a very weak mixing of terms while the $^1F_3^o$, $^3F_3^o$ and the $^3D_3^o$ levels exhibit a strong mixing of the corresponding terms. However, in each case the assigned label reflects the dominant composition. In the case of the $3p^55s$ configuration, the composition of the two $^1P_1^o$ and $^3P_1^o$ levels is highly mixed, much more so than for the levels of the corresponding $3p^54s$ configuration. Since the spin–orbit interaction comes from the same $3p^5$ subshell, the smaller mixing for the levels of $3p^54s$ can be attributed to the larger separation of the non-relativistic terms due to a the larger exchange and larger core-polarization effect. Thus with only two exceptions, the labels in LSJ correspond to the dominant LS component of the wavefunction.

In table 3 we compare the length and velocity forms of the line strength in the core-polarization models, Breit–Pauli and MCDHF, for several transitions. As in table 1, we notice

Table 4. Optimization strategies for groups of term. Eigenfunctions are designated by the dominant configuration for each term.

Group	Even		Group	Odd	
	Configuration	Term (s)		Configuration	Term (s)
1	$3p^6$	1S	1	$3p^5 4s$	$^1P^o, ^3P^o$
2	$3p^5 4p$	$^1P, ^3P, ^1D, ^3D$	2	$3p^5 3d$	$^1D^o, ^3D^o, ^1F^o, ^3F^o,$ $^1P^o(0.3), ^3P^o(0.3)$
3	$3p^5 4p$	3S			
4	$3p^6$	$^1S(0.3)$		$3p^5 4s$	$^1P^o(0.3), ^3P^o(0.3)$
	$3p^5 4p$	1S		$3p^5 5s$	$^1P^o(0.3), ^3P^o(0.3)$
			3	$3p^5 3d$	$^1P^o, ^3P^o, ^1D^o(0.3),$ $^3D^o(0.3)$
				$3p^5 4s$	$^1P^o(0.3), ^3P^o(0.3)$
				$3p^5 5s$	$^1P^o, ^3P^o$

that the two forms of the line strengths are in better agreement for transitions between excited states than for transitions from the ground state. Moreover, the length and velocity forms of the MCDHF and Breit–Pauli line strengths for the $3p^5 4s \rightarrow 3p^5 4p$ and $3p^5 4s \rightarrow 3p^5 3d$ transitions are in quite good agreement with each other, while they differ for transitions from the ground state. These results suggest that a more appropriate computational model is necessary for spectrum calculations that included the ground state.

4. Extended correlation model

Using the experience gained from the Breit–Pauli core-polarization calculation, a second calculation was performed that included more extended correlation. Expansions were generated using single (S) and double (D) excitations from a multi-reference set of configuration states. The $1s^2 2s^2 2p^6$ subshells were treated as an inactive core while the remaining six electrons in outer shells were considered to be active (valence electrons). Wavefunction expansions were obtained from orbital sets of increasing size where $3 \leq n \leq 7$, so that convergence could be monitored. Those configurations from SD excitation expansions which did not interact with at least one member of the multi-reference set were discarded.

In this model, the expansions are considerably larger and it was now necessary to optimize the orbitals for smaller sets of LS terms. Because the Breit–Pauli interaction matrix needs to be computed from one orthonormal orbital basis, LS terms were grouped according to the term interaction shown in table 2: whenever there was an interaction between two terms, the two terms needed to be in the same group. Simultaneous optimization of the radial functions was performed on all LS states that were grouped together. This grouping is described in table 4. For each group, the listed configurations and terms defined the multi-reference set for the different terms. The desired LS states are those for which the default weight is unity (unspecified). Thus in the fourth even group, for example, the 1S expansion was obtained from SD excitations from $3p^6$ and $3p^5 4p$ and during the optimization process, the first 1S eigenstate was weighted by a somewhat arbitrary, small factor of 0.3 whereas the second had a weight of unity. Thus the first eigenstate is not totally ignored, even though the second eigenstate is the desired result from this calculation. For the second odd group, there were multiple terms for which wavefunctions were to be determined, some of which were for higher eigenstates. Consequently the multi-reference set for $^1P^o$, for example, included the three configurations

Table 5. Comparison of relativistic line strengths in the extended correlation model. Per cent differences were computed according to the formula $[S(l) - S(v)] \times 100/S(l)$.

	$S(l)$	$S(v)$	Difference (%)	$S(l)$	$S(v)$	Difference (%)
	$3p^6\ ^1S_0 - 3p^54s\ ^1P_1^o$			$3p^54s\ ^3P_2^o - 3p^54p\ ^3D_3$		
<i>Ab initio</i>	0.913	0.911	0	66.66	66.62	0
Adjusted	0.919	0.909	1	66.56	66.21	1
	$3p^6\ ^1S_0 - 3p^53d\ ^1P_1^o$			$3p^54p\ ^3P_2 - 3p^53d\ ^3D_2^o$		
<i>Ab initio</i>	0.381	0.357	6	11.90	11.65	2
Adjusted	0.427	0.397	7	15.08	14.46	4

$3p^53d$, $3p^54s$ and $3p^55s$. Generally, all the terms of a configuration are designated as a group, but in the present case, this resulted in expansions that were too long and weak interactions suggested that some could be dealt with separately. In addition, a strong Coulomb interaction, as in $3p^53d$ and $3p^55s\ ^1P_1^o$ and $^3P_1^o$, required that the two eigenstates be in the same group.

Once radial functions had been determined for each group, the Breit–Pauli CI calculations were performed and transition data determined from these wavefunctions. All E1 transitions between odd and even levels were computed as well as E2 and M1 transitions between the $3p^54p$ group of levels, though their effect on lifetimes is negligible. Energy levels relative to the ground state were now generally too low by between 400 and 500 cm^{-1} with several considerably lower and a few higher. In order to improve the reliability of the mixing of LS terms in the Breit–Pauli interaction matrix, adjustments were made to the matrix elements that shifted all diagonal components of a given LS block by a fixed amount. This shift was the difference of an *ab initio* energy level and the observed level for either the highest or lowest J value in the case of triplets. In this process, the terms in an optimization group (see table 4) were adjusted together. If more than one eigenstate in a group had the same LS value as, for example, $3p^53d\ ^1P_1^o$ and $3p^55s\ ^1P_1^o$ in the odd group 3, energy adjustments were made separately for each of the eigenstates with different shifts for $^1P_1^o$. Because of the strong interactions between terms, adjustments often needed to be repeated. The extreme J was selected because this component does not interact with the corresponding singlet term and our experience showed that adjustments converged faster in this scheme compared with making adjustments to the same J for both triplet and singlet levels of an LS term.

In table 5, we report both *ab initio* and adjusted line strengths in the Breit–Pauli extended correlation model. Compared with core-polarization line strengths for ground state transitions, the extended correlation model results are in much better agreement both for *ab initio* and adjusted data. For example, the length and velocity forms of the line strength for $3p^6\ ^1S_0 \rightarrow 3p^54s\ ^1P_1^o$ differ by less than 1%, while in the core-polarization model this disagreement was 34%, for $n = 8$, as shown in table 1. The length form of the line strength is independent of energy and it is interesting to note that extended correlation has reduced this value by 5%.

The results of our adjusted extended correlation calculations are presented in table 6. Included are energies relative to the ground state, computed – observed [26] energy differences, the splitting within multiplets relative to the energy of the lowest and the lifetimes of the levels. In comparison with the core-polarization model, energies in the correlation model are in much better agreement with observed energies, even before the adjustment. In the case of multiplets, the smallest difference indicates the level used in the adjustment process. For example, in $3p^54p\ ^3P$ the multiplet was shifted for agreement with observed for $J = 0$. The difference with observed for 3P_2 and 3P_1 of 96 cm^{-1} and $-11\ \text{cm}^{-1}$, respectively, is a reflection

Table 6. Breit–Pauli extended correlation model energies, energy differences (computed – observed) in cm^{-1} , splittings and lifetimes in s for excited states up to and including $3p^5 3d^1 P_1^0$ after adjustment.

Configuration	Term	Level	Difference	Splitting	Lifetime
$3p^6$	1S_0	0.00	0.00		
$3p^5 4s$	$^3P_2^o$	93163.5	19.71		
	$^3P_1^o$	93756.1	5.50	592.62	9.6479×10^{-9}
	$^3P_0^o$	94469.0	-84.71	1305.49	
	$^1P_1^o$	95394.3	-5.51		1.8564×10^{-9}
$3p^5 4p$	3P_1	104108.1	5.97		3.8989×10^{-8}
	3D_3	105468.7	5.97		2.7861×10^{-8}
	3D_2	105701.2	83.87	232.42	2.8986×10^{-8}
	3D_1	106126.3	39.04	657.57	2.7753×10^{-8}
	3P_2	106333.4	95.86		2.6448×10^{-8}
	3P_0	107054.2	-0.02	720.84	2.3120×10^{-8}
	3P_1	107486.1	-10.33	1152.68	2.6208×10^{-8}
	1P_1	107120.9	-10.83		2.7302×10^{-8}
	1D_2	107294.1	4.41		2.7602×10^{-8}
	1S_0	108727.3	4.69		2.1645×10^{-8}
$3p^5 3d$	$^3P_0^o$	111667.7	-0.09		7.9795×10^{-8}
	$^3P_1^o$	111808.1	-9.98	140.37	6.8002×10^{-8}
	$^3P_2^o$	112102.3	-36.63	434.61	8.7573×10^{-8}
	$^3F_4^o$	112769.5	19.34		5.8425×10^{-8}
	$^3F_3^o$	113020.8	0.48	251.35	5.6936×10^{-8}
	$^3F_2^o$	113420.1	-5.87	650.60	5.5190×10^{-8}
	$^3P_2^o$	113549.5	81.04		3.2025×10^{-8}
$3p^5 5s$	$^3P_0^o$	114848.3	-13.38	1298.75	3.3040×10^{-8}
	$^3P_1^o$	114912.5	-62.53	1362.98	1.5199×10^{-8}
	$^1P_1^o$	113648.3	5.03		8.3089×10^{-9}
$3p^5 3d$	$^1F_3^o$	113721.4	4.86		5.2151×10^{-8}
	$^3D_1^o$	114189.8	42.06		3.0558×10^{-9}
	$^3D_3^o$	114759.1	-62.86	569.29	5.1537×10^{-8}
	$^3D_2^o$	114834.5	29.40	644.75	4.9616×10^{-8}
	$^1D_2^o$	114608.3	-32.71		5.2464×10^{-8}
	$^1P_1^o$	115364.9	-1.94		2.1639×10^{-9}

of the fact that our calculations have not accurately captured the fine-structure splitting. In some instances, such as $3p^5 5s^3 P^o$, close agreement could not be obtained. Similarly, the energy adjustment for the level $3p^5 3d^1 P_1^o$ was not successful. As was already noted in other studies [27], we make the remark that the calculation of atomic data involving this term can be particularly difficult.

Our scheme for monitoring the accuracy of transition probabilities has already been described [23, 28, 29]. This mechanism relies on comparison of the length and velocity gauges of LS allowed transitions, as well as on transition energy accuracies. A few selected transition probabilities are displayed in table 7; other transition data can be obtained from a

Table 7. Selected Ar I transition probabilities (in s^{-1}) in the Breit–Pauli extended correlation model^a.

Transition	<i>Ab initio</i>		Adjusted	
	$A_{ki}(l)$	$A_{ki}(v)$	$A_{ki}(l)$	$A_{ki}(v)$
$3p^6\ ^1S_0 - 3p^54s\ ^1P_1^o$	5.2783×10^8	5.2677×10^8	5.3866×10^8	5.3272×10^8
$- 3p^54s\ ^3P_1^o$	1.0568×10^8	1.0863×10^8	1.0365×10^8	1.0561×10^8
$- 3p^55s\ ^1P_1^o$	8.9173×10^7	8.9581×10^7	9.5170×10^7	9.4717×10^7
$- 3p^53d\ ^3D_1^o$	3.3813×10^8	3.2484×10^8	3.0753×10^8	2.9345×10^8
$3p^54s\ ^3P_0^o - 3p^54p\ ^3S_1$	1.0847×10^6	1.3513×10^6	1.1046×10^6	1.4639×10^6
$3p^54s\ ^3P_1^o - 3p^54p\ ^3S_1$	5.8259×10^6	6.6709×10^6	5.4985×10^6	6.6200×10^6
$3p^54s\ ^3P_2^o - 3p^54p\ ^3S_1$	2.0495×10^7	2.2079×10^7	1.8870×10^7	2.1210×10^7
$3p^54s\ ^1P_1^o - 3p^54p\ ^1S_0$	5.0255×10^7	5.5509×10^7	4.6084×10^7	5.3843×10^7
$3p^54p\ ^3S_1^o - 3p^53d\ ^3P_0$	1.1552×10^7	1.0483×10^7	1.0884×10^7	1.0197×10^7
$3p^54p\ ^3S_1^o - 3p^53d\ ^3P_1$	1.0071×10^7	9.1232×10^6	9.6526×10^6	8.9740×10^6
$3p^54p\ ^3S_1^o - 3p^53d\ ^3P_2$	6.1129×10^6	5.6060×10^6	5.9541×10^6	5.5303×10^6
$3p^54p\ ^3S_1^o - 3p^55s\ ^1P_1$	3.8981×10^6	2.8098×10^6	4.0750×10^6	2.6877×10^6
$3p^54p\ ^3D_1^o - 3p^55s\ ^1P_1$	5.1195×10^6	5.3857×10^6	4.6652×10^6	4.8027×10^6
$3p^54p\ ^3D_2^o - 3p^55s\ ^1P_1$	1.1803×10^7	1.1878×10^7	1.0174×10^7	9.9939×10^6
$3p^54p\ ^3P_2^o - 3p^53d\ ^1F_3$	1.5336×10^7	1.4800×10^7	1.4682×10^7	1.5079×10^7
$3p^54p\ ^1P_1^o - 3p^53d\ ^3F_1$	7.8898×10^4	9.4038×10^4	7.8338×10^4	1.0240×10^5
$3p^54p\ ^1P_1^o - 3p^53d\ ^1D_2$	1.7066×10^7	1.6389×10^7	1.5394×10^7	1.5567×10^7
$3p^54p\ ^1D_2^o - 3p^55s\ ^3P_1$	1.1912×10^7	1.2493×10^7	1.2480×10^7	1.2968×10^7
$3p^54p\ ^1D_2^o - 3p^55s\ ^3P_2$	1.3368×10^5	2.1806×10^5	1.5848×10^5	2.4406×10^5
$3p^54p\ ^1D_2^o - 3p^53d\ ^1D_2$	2.2685×10^6	2.1910×10^6	2.1180×10^6	2.1947×10^6

^a The velocity form of the transition operator has neglected some relativistic corrections and hence, unlike the length form, is not correct in that some terms of order α^2 have been omitted. The values of the length and velocity gauges have significance when term mixing is small and the transition is spin-allowed.

web database [30]. The adjusted values have been computed with more accurate transition energies, but on the whole it is not clear that length and velocity values are in better agreement.

Table 5 has already shown that this extended correlation model improved the agreement in the length and velocity form of the line strength of some transitions from the ground state. In table 8 we compare the length and velocity weighted oscillator strengths for some transitions between excited states for all our computational models. Let us first compare the two core-polarization results. The models for these two calculations were the same, but the optimization procedures were different in that only new orbitals could be optimized in MCDHF as the expansion increased. Though table 2 showed better excitation energies for MCDHF than the present Breit–Pauli, the length and velocity gauges of the latter are generally better for these transitions. In the extended correlation model, the difference between the *ab initio* and energy adjusted results is an indication of uncertainty. In several instances, the adjusted values have better agreement between length and velocity forms suggesting they are the more reliable. The last transition, $3p^54p\ ^1S_0 \rightarrow 3p^55s\ ^1P_1^o$, cannot be considered reliable, though there is agreement between the MCDHF core-polarization values and the Breit–Pauli extended correlation ones. The effect of adding core–core correlation to core-polarization is often between 5 and 10% but it has increased the oscillator strength by 26% for the $3p^54p\ ^3S_1 \rightarrow 3p^53d\ ^3P_2^o$ transition.

Table 8. Selected weighted relativistic oscillator strengths (gf values) for transitions between excited states from our different theoretical models.

Gauge	Core-polarization		BP extended correlation	
	MCDHF	BP	<i>Ab initio</i>	Adjusted
	$3p^5 4s \ ^3P_2 - 3p^5 4p \ ^3D_3^o$			
gf (l)	2.36	2.35	2.49	2.48
gf (v)	2.37	2.41	2.48	2.47
	$3p^5 4p \ ^3P_1 - 3p^5 3d \ ^3P_2^o$			
gf (l)	0.545	0.519	0.703	0.698
gf (v)	0.452	0.515	0.645	0.649
	$3p^5 4p \ ^3D_3 - 3p^5 3d \ ^3F_3^o$			
gf (l)	0.422	0.398	0.482	0.486
gf (v)	0.373	0.395	0.458	0.485
	$3p^5 4p \ ^1D_2 - 3p^5 3d \ ^1D_2^o$			
gf (l)	0.274	0.265	0.298	0.297
gf (v)	0.254	0.264	0.288	0.308
	$3p^5 4p \ ^1S_0 - 3p^5 5s \ ^1P_1^o$			
gf (l)	0.041	0.064	0.040	0.040
gf (v)	0.117	0.060	0.144	0.112

5. Comparison with experiment and other theory

The resonance transitions, $3s^3 3p^6 \ ^1S_0 \rightarrow 3p^5 4s \ ^1,3P_1^o$ have a long history going back as far as 1958. (An extensive list of references to experimental and theoretical data can be found in [11] and [19].) In table 9, we analyse recent theoretical values and experimental data for these transitions more closely. In addition to f-values, we also look at the ratio of the f-values for the allowed and spin-forbidden transitions. It appears that experiment can determine this ratio more accurately than the f-values themselves. For the upper levels, we also compare with observed g_J factors which depend largely on the term composition of a level.

For theory, there are a number of accuracy indicators. In addition to the excitation energy, there is the energy separation between the $^1P_1^o$ and $^3P_1^o$ levels which was 1617 cm^{-1} in our *ab initio* Breit–Pauli calculation and adjusted to 1638 cm^{-1} . Another is the spread of the $^3P^o$ multiplet which was 1305.40 cm^{-1} (not affected by adjusting) compared to 1413.91 cm^{-1} for the observed. This suggests that the relativistic effect was not large enough, and that the mixing of the $^1P_1^o$ and $^3P_1^o$ terms was too small. This is confirmed by the g_J factor that is too large for 3P_1 and too small for 1P_1 .

We therefore also undertook an extended correlation MCDHF calculation for these transitions. Expansions were obtained through SD excitations $3s^2 3p^6$ and $3s^2 3p^5 4s$ for odd and even states, respectively, for $n = 3, 4, 5$. For the odd levels, calculation (a) proceeded with the same scheme also for $n = 6$, but (b) added only core-polarization CSFs that emphasize the outer region of the wavefunction important in transition probabilities. The results are reported in table 9 and compared with experiment, first for energies and then for f-values. The Breit–Pauli (BP) energy is for the *ab initio* energy. Comparing with MCDHF, the relativistic configuration interaction (RCI) performed by Avgoustoglou and Beck [19], and the most recent configuration interaction and relativistic many-body perturbation theory (CI+RMBPT) by Savukov [20], the MCDHF (b) energies are the best with the present Breit–Pauli (BP) a close second but the computed g_J for the latter are not in good agreement with observed.

Table 9. A detailed comparison of $3p^6\ ^1S_0 \rightarrow 3p^54s\ ^1,^3P_1^o$ with recent theory and experiment.

Method	Energies			gJ	
	$^3P_1^o$	$^1P_1^o$	Difference	$^3P_1^o$	$^1P_1^o$
Obs. [26]	93751	95400	1649	1.404	1.102
BP (present)	93346	94963	1617	1.416	1.085
MCDHF (a)	92811	94407	1596	1.400	1.101
MCDHF (b)	93438	95089	1606	1.402	1.098
RCI [19]	94526	96238	1712		
CI+RMBPT [20]	92595	95307	1712		
f-values					
Source	$^3P_1^o$	$^1P_1^o$	Ratio		
Experiment					
Federman <i>et al</i> [9]	0.064	0.257	4.01		
Chan <i>et al</i> [32]	0.0662(33)	0.265(13)	4.00		
Ligtenberg <i>et al</i> [11]	0.0616(21)	0.2297(93)	3.73		
Wu <i>et al</i> [10]	0.0676(40)	0.2590(150)	3.83		
Gibson and Risley [12]	0.0580(17)	0.2214(68)	3.82		
Theory					
BP (fine tuned)	0.0619	0.2662	4.30		
MCDHF (a)	0.0570	0.221	3.87		
MCDHF (b)	0.0562	0.226	4.02		
RCI [19]	0.0672	0.248	3.69		
CI+RMBPT [20]	0.0629	0.254	4.03		

In the study of f-values, Federman *et al* [9] measured the f-value for the allowed transition but used semi-empirical methods for estimating the value for the intercombination line and noted that the ratio of allowed to forbidden was about 4.0. Since then, there have been several accurate experimental measurements, and though the absolute values for their f-values differ, the ratios are considerably more constant, generally in the range of 3.8–4.0.

In our Breit–Pauli calculations the spread of the $^3P^o$ term is too small, in that the separation between $^3P_2^o$ and $^3P_0^o$ is too small, suggesting that the relativistic correction is too small. If the Breit Pauli f-values are also corrected for the spread of the levels (as suggested by Hibbert in a process referred to as ‘fine-tuning’ [31]) we get the values in the table, with a ratio of 4.3. The MCDHF and CI+RMBPT theoretical ratios are in good agreement with the experimentally determined ones, but the MCDHF f-values from calculations (a) are the closest to the experimental values of Gibson and Risley that have the smallest error bars. The ratio for the RCI value is too low. The considerable difference in the present Breit–Pauli and MCDHF f-values for the allowed transition suggests relativistic effects were not captured accurately by the Breit–Pauli approximation.

A few recent papers have included some transitions to $3p^53d\ ^3P_1^o, ^3D_1^o$ and $^1P_1^o$ and $3p^55s\ ^3P_1^o$ or $^1P_1^o$. In table 10, we compare our oscillator strengths for these transitions with experiment and with some theory from the 1970s. The present theory on the whole is more accurate than the quantum defect theory of 1974 [17]. What is interesting is that in going from 4s to 5s the ratio of the oscillator strength of $^1P_1^o$ to $^3P_1^o$ changes from about 4.0 to 2.0 for the experimental values due to the larger mixing in the two 5s levels.

Using a laser gas-discharge, Savukov and Berry [13] measured the ratio of line strengths of two transitions from the $3p^54s\ ^1P_1^o$ excited state. The transitions with wavelengths of 9787 Å and 9227 Å were to $3p^53d\ ^3D_2^o$ and $^3P_2^o$ levels, respectively. For transitions between excited

Table 10. Comparison of f-values for some transitions from the ground state to $3p^5 3d$ and $3p^5 5s$ levels.

Source	f-values				
	$3d\ ^3P_1^o$	$5s\ ^1P_1^o$	$3d\ ^3D_1^o$	$5s\ ^3P_1^o$	$3d\ ^1P_1^o$
Experiment					
Wu <i>et al</i> [10]	0.0010(3)	0.0241(29)	0.0929(78)	0.0122(32)	0.106(10)
Chan <i>et al</i> [32]	0.0013(1)	0.0264(26)	0.0914(91)	0.0126(13)	0.109(11)
Theory					
BP <i>ab initio</i>	0.0011	0.0314	0.1175	0.0191	0.1330
BP <i>adjusted</i>	0.0009	0.0331	0.1061	0.0135	0.1496
Lin <i>et al</i> [18]	0.0037		0.049		0.167
Lee [17]	0.0016	0.045	0.045	0.039	0.128

Table 11. Comparison of line strengths for some transitions from the $3p^5 4s\ ^1P_1^o$ to $3p^5 4p\ ^3D_2$ and 3P_2 levels.

Method	Line strength		Ratio
	$3p^5 4p\ ^3D_2^o$	$3p^5 4p\ ^3P_2^o$	
Core-polarization			
BP	3.30	12.42	3.76
MCDHF	3.32	10.80	3.25
Extended correlation			
BP <i>ab initio</i>	4.387	11.68	2.66
BP <i>adjusted</i>	1.617	10.82	6.69

states, the core-polarization results are applicable, and in table 11 we compare our four ratios. The experimental value for the ratio was 3.29(13), a value that had been confirmed by a theoretical value of 3.23 [13]. In the core-polarization model, the MCDHF ratio with the value of 3.25 is in excellent agreement with experiment, whereas in the extended correlation model, the *ab initio* ratio is too small and the adjusted ratio much too large. The adjustment has brought the line strength for the transition from $3p^5 4p\ ^3P_2$ into excellent agreement with the MCDHF value, but the line strength for 3D_2 was reduced by more than a factor of 2. As table 2 showed, the composition of the $3p^5 4p\ ^3D_2$ and 3P_2 levels is highly mixed, also involving a 1D_2 component. Small adjustments to the energy result in considerable changes in composition and transition probabilities, some being more sensitive to change than others. The most reliable calculation in this case appears to be the MCDHF core-polarization method.

6. Conclusions

Breit–Pauli and multiconfiguration Dirac–Hartree–Fock energy levels and E1 and some E2 and M1 transition probabilities were computed for neutral argon. The core-polarization model was useful for determining the mixing of terms in Ar I. As a result of this process, terms were grouped together based on their term mixing. A Breit–Pauli correlation model including SD excitations was then applied, which yielded energy levels from the ground state in significantly better agreement with experiment. In the case of the resonance transition, the MCDHF results were in better agreement with experiment than the Breit–Pauli results, in spite of the fact that argon is a relatively light, neutral atom. Breit–Pauli results were best for *J*-values where

term mixing was relatively small. For wavefunctions with a highly mixed composition, the diagonal energy adjustment could produce large changes in transition probabilities and was deemed not reliable.

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