PHYSICAL REVIEW A VOLUME 34, NUMBER 3 SEPTEMBER 1986

Energy levels and lifetimes for some core-excited quartet states in Na I and Mg II

Charlotte Froese Fischer*
Physics Division, Argonne National Laboratory, Argonne, Illinois 60439

(Received 11 April 1986)

Multiconfiguration Hartree-Fock calculations with Breit-Pauli relativistic corrections are reported for the metastable core-excited quartet states $2p^5 3s\,3p$, $2p^5 3s\,3d$, and $2p^5 3s\,4s$ in Na I and Mg II, and also for $2p^5 3p^2$ in the latter. Both correlation and relativistic effects play an important role, as expected, but in addition it was found that term dependence of the radial functions was important. In Na I the latter tended to reduce the mixing of the different terms. Lifetime determination of the odd quartets included decay to $2p^5 3s3p$, $2p^6 3s$, and $2p^6 3d$ levels as well as autoionization. The resulting lifetimes of several levels in Na I are in somewhat better agreement with experiment than those reported from other theories.

I. INTRODUCTION

The core-excited quartet levels of Na I and Mg II are metastable against autoionization. For this reason they are of interest in atomic spectroscopy and also in the construction of xuv lasers. Recently, Holmgren *et al.*[1] established a number of core-excited Na levels in spectra obtained with a pulsed hollow-cathode discharge. Each level was confirmed by observing enhanced fluorescence when the population of the upper level was selectively increased through the use of a laser. They also proposed three possible xuv lasers, but only two transitions were identified. Their experimental analysis was supported through theoretical calculations using Cowan's RCN/RCG code,[2] based on a multiconfiguration Hartree-Fock model with empirically adjusted Slater parameters. The lifetimes predicted by these calculations were tested experimentally by Engström *et al.*,[3] using the beam-foil technique. Agreement between theory and experiment was within a factor of 2.

The $2p^5 3snl$ levels of the sodium sequence also are interesting from a theoretical point of view. Like the Mg sequence, which has been investigated earlier[4] and where the $2p$ shell is filled, correlation in the motion of the outer two electrons will result in substantial mixing of configurations. The best-known example is the mixing of $3s3d\,^1D$ and $3p^2\,^1D$; this configuration mixing accounts for the fact that in Mg I the ^1D state is *lower* than the ^3D. In Mg I there was substantially less mixing of configurations in the triplet states than the singlet states.

The core-excited quartet states of Na I are similar, in some respects, to the triplet states of Mg but with the $2p^6$ core replaced by $2p^5$ and the nuclear charge reduced by one. However, when relativistic effects are included there is an important difference: the unfilled $2p$ shell produces spin-orbit interactions which mix the different terms of the configuration (the spin-orbit parameters for the outer electrons are negligible in comparison to the $2p$ parameter). Thus a theoretical prediction of energy levels and lifetimes will need to deal adequately with both correlation and relativistic effects simultaneously.

In this paper, multiconfiguration Hartree-Fock (MCHF) results with relativistic effects included through the Breit-Pauli (BP) approximation[5] are reported. Unlike a nonrelativistic MCHF calculation,[6] this approach is not a strictly variational one. In some respects, this is a disadvantage—a disadvantage that could only be overcome by a fully relativistic multiconfiguration Dirac-Fock (MCDF) calculation[7,8] for each level. Such calculations tend to be extensive and fine-structure splittings may not be accurate for the neutral atom or ions of low degree of ionization.[9] On the other hand, the MCHF + BP method does provide a mechanism for determining a *portion* of a spectrum in a single calculation, a portion that may contain many levels. In this approach, the first stage is an MCHF calculation to determine a basis for the representation of the states of interest. The next stage is a configuration-interaction calculation within the Breit-Pauli approximation neglecting orbit-orbit interactions which are expected to be small. The eigenvalues of the interaction matrix represent the total energy of the system and the eigenvectors, the wave-function expansion.

II. WAVE-FUNCTION COMPUTATION

Initially, Hartree-Fock calculations were performed for $2p^5 3s\,^3P$; the $1s$, $2s$, and $2p$ functions obtained from this calculation were then kept fixed throughout all further studies.

Next, the term dependence of the $2p^5 3s3p$ and $2p^5 3s3d$ configurations was investigated in the fixed-core, Hartree-Fock approximation. The mean radii of the outer electrons for all terms of these two configurations are reported in Tables I and II, respectively. The pattern of behavior is similar, though relatively more pronounced for the $2p^5 3s3p$ configuration of Table I.

The coupling scheme used in these calculations is the left-to-right coupling of the shells. That is, first the $3s$ electron is coupled to the $2p^5$ shell to yield either a ^3P or ^1P intermediate term, and then the outer electron couples to it to yield the final-term value. It is interesting to note that the mean radii for the $3s$ electron do not depend primarily on the intermediate coupling. In fact, the mean radii of either the outer $3p$ or $3d$ electron for the $(^3P)\,^4L$

TABLE I. Variations in the Hartree-Fock mean radius of $3s$ and $3p$ electrons in the $2p^5 3s(^{1,3}P)3p$ LS configuration of Na showing the term and coupling dependence.

Term	$\langle r_{3s} \rangle$		$\langle r_{3p} \rangle$	
	(^3P)	(^1P)	(^3P)	(^1P)
^4S	3.250		3.948	
^4P	3.240		4.258	
^4D	3.244		4.135	
^2S	2.975	3.301	6.378	4.541
^2P	3.005	3.302	5.933	4.554
^2D	3.011	3.313	5.818	4.429

terms are essentially the same as those for (^1P) ^2L. Only for the (^3P) ^2L couplings is there an appreciable difference. In this case, the outer electron moves further out and the $3s$ electron moves closer to the nucleus. Apparently the (^1P) ^2L coupling prevents the $3s$ from moving closer to the nucleus, and so the outer electron does not move out as much as one would expect in going from a quartet to a doublet.

Though the main interest in this study is in the quartet states, because of the spin-orbit interaction, it is important also to represent the different doublet states with reasonable accuracy. For this reason, a "mixed" approach was taken to the determination of a radial basis. We shall describe the procedure for each of the configurations. For convenience the $2p^5$ shell will frequently be omitted from the notation for a configuration.

A. $2p^5 3s 3p$

First, a fixed-core Hartree-Fock calculation was performed for $3s_1(^3P)3p_1$ ^2S. Then, with the $3s_1$ and the $3p_1$ orbitals fixed, an MCHF calculation was performed for a wave-function expansion over the set of configuration states

$$\{3s_1 3p_1,\ 3s_1 4p_1,\ 4s_1 3p_1,\ 4s_1 4p_1,\ 3p_2 3d_2\ ,$$
$$3p_2 4d_2,\ 4p_2 3d_2,\ 3d_3 4f_3\}\ ^4S\ .$$

Note the use of different radial functions for the different angular couplings. In this form the $3d_2$ and $4p_2$ orbitals were not well determined, both being associated with small components of the wave function.

TABLE II. Variations in the Hartree-Fock mean radius of $3s$ and $3d$ electrons in the $2p^5 3s(^{1,3}P)3d$ LS configuration of Na showing the term and coupling dependence.

Term	$\langle r_{3s} \rangle$		$\langle r_{3d} \rangle$	
	(^3P)	(^1P)	(^3P)	(^1P)
^4P	3.004		9.225	
^4D	2.999		9.524	
^4F	3.002		9.336	
^2P	2.964	3.076	10.393	9.629
^2D	2.963	3.073	10.532	9.853
^2F	2.964	3.075	10.418	9.692

For the Breit-Pauli wave-function expansion, the $4p_2 3d_2$ configuration was omitted, but all couplings and final terms were included which had a final J value in common with at least one of the terms of $2p^5 3s 3p$. Not all Breit-Pauli operators were included for interactions with the $3d_3 4f_3$ configuration. For these interactions, only the electrostatic, the J-independent relativistic corrections (mass correction, Darwin term, and spin-spin contact), and spin-orbit operators were included in the calculation, since the other effects were expected to be small.

B. $2p^5 3s 3d$

First, $3s_1$ and $3d_1$ radial functions were obtained from a fixed-core Hartree-Fock calculations for $3s_1(^3P)3d_1$ ^2P. Then, with these functions fixed, an MCHF calculation was performed for the wave-function expansion

$$\{3s_1 3d_1,\ 3s_1 4d_1,\ 4s_1 3d_1,\ 4s_1 4d_1,\ 3s_1 4s_1\ ,$$
$$3d_2 4d_2,\ 3d_2^2, 4d_2^2\ , 3p_2 4p_2,\ 3p_2^2,\ 4p_2^2,\ 3p_3 4f_3\ ,$$
$$4p_3 5f_3, 4f_3^3,\ 3s_1 5d_1,\ 3s_1 5s_1\}\ ^4P\ .$$

The Breit-Pauli expansion now included all possible terms of the above list of configurations with a J value in common with at least one of the terms of $2p^5 3s 3d$, as well as the $2p^5 3s^2$ configuration. The result was an expansion over 252 configuration states. Since the evaluation of the two-body Breit-Pauli operators is a lengthy, CPU intensive process that cannot be vectorized on the CRAY computer, the configurations were ordered according to their importance, as follows. For 0,

$$\{3s_1 3d_1,\ 3s_1 4d_1\}\ .$$

For 1,

$$\{4s_1 3d_1,\ 4s_1 4d_1,\ 3s_1 5d_1,\ 3p_3 4f_3\ , 3p_2 4p_2,\ 3p_2^2,\ 4p_2^2\}\ .$$

For 2,

$$\{3s_1^2,\ 3s_1 4s_1,\ 3s_1 5s_1,\ 3d_2^2,\ 3d_2 4d_2\ , 4d_2^2,\ 4f_3^2,\ 4p_3 5f_3\}\ .$$

All the relativistic operators (except the orbit-orbit operator which was neglected in all cases) were evaluated between members of what may be thought of as the zero-order set. All the operators also were evaluated for interactions between members of the zero-order set and the first-order set. All J-independent relativistic corrections were included for the remaining interactions but J-dependent interactions were restricted. Within the first-order set, only the spin-orbit interaction (as defined by Glass and Hibbert[10]) was included for interactions between configurations, though all operators were evaluated for the diagonal contributions. For the second-order set, in all cases only the spin-orbit operator was evaluated.

C. $2p^5 3s 4s$

The $2p^5 3s 4s$ configuration has the same parity as $2p^5 3s 3d$ and, for certain terms, there is an electrostatic interaction between them. However, the interaction is relatively small in Na I and so the correlation orbitals obtained in the MCHF calculation for the latter might not be a good representation of the states for which $2p^53s4s$ is the dominant configuration. The $3s_15s_1$ configurations were included in the wave-function expansions for the $2p^53s3d$ odd parity states, to allow for changes in the outer orbitals of the two configuration states. In fact, in Na I the nonrelativistic energy of the $2p^53s4s\,^4P$ state was lower by only 0.000 10 a.u. when all radial functions were varied (using the same expansion as for the nonrelativistic MCHF calculations described earlier for $2p^53s3d$ but a different dominant component) than when only the $5s_1$ and $5d_1$ functions were varied. The effect was somewhat larger in Mg II. For the latter, a basis was used that allowed all orbitals to vary other than the $3s_1$, $4s_1$, $3d_1$, $4d_1$ orbitals. In this way, the basis was tuned to the $2p^53s4s$ states, but at the same time was able to represent the $2p^53s3d$ states adequately to allow for interactions with these configurations.

D. $2p^53p^2$

The $2p^53p^2$ quartets are high-lying states in Na I, but in Mg II the $2p^53p^2(^1D)\,^2L$ states are lower than the $2p^53snl$ odd quartets, $nl=4s$ or $3d$. The same Breit-Pauli wave-function expansion was used as for the $2p^53s4s$ states, but the interaction matrix was redefined to include *all* relativistic interactions between the $3p_2^2$, $3p_24p_2$, and $4p_2^2$ configurations. (It was verified that these interactions were not important for the other configuration states considered earlier.) The radial functions were determined from an MCHF calculation for the $2p^53p^2(^3P)\,^4P$ state, again with the same wave-function expansion as for the $2p^53s3d\,^4P$ state given earlier, but with a different dominant component. In this calculation, the $3s_1$ and $3d_1$ orbitals were kept fixed.

The calculations described above have used a nonorthogonal basis—for example, the $3p_1$ orbital describing the configuration $2p^53s3p$ is not the same as the $3p_2$ orbital describing $2p^53p3d$. By allowing orbitals to depend on the angular quantum numbers of the electrons, it is possible to capture correlation effects with fewer configurations. Such nonorthogonality complicates the evaluation of interaction matrix elements. The present programs can deal with this complexity only in the evaluation of electrostatic interactions. Of the relativistic Breit-Pauli operators, the most important one is the nuclear spin-orbit operator, a one-electron operator which contributes only when the two configurations differ by a single electron with the same orbital angular quantum number. The configuration states in the above Breit-Pauli wave-function expansion are always orthonormal within a given "angular" configuration. For example, the radial functions of all p^5sd configurations are orthonormal. The Breit program which assumes an orthonormal basis will compute interactions correctly within these configurations, but not between different angular configurations. The latter are present in the wave-function expansion because of their importance due to correlation. Since there will be no spin-orbit interaction between them, the relativistic correction will be small. The Breit program[11] would produce integrals for the two-body operators in a manner equivalent to assuming the $2p^5$ shell is not involved in the interaction.

III. WAVE-FUNCTION COMPOSITIONS

In Tables III—V are reported the larger wave-function expansion coefficients for the $2p^53s3p$, $2p^53s3d$, and $2p^53s4s$ quartets, respectively, for both Na I and Mg II. The coefficients are for the more traditional term-dependent basis rather than the mixed basis that was in

TABLE III. Composition of $2p^53s3p$ quartet states in Na I and Mg II.

Term	Wave-function expansion		
		Na I	
$^4S_{3/2}$	0.98 $(^3P)3p\,^4S$	-0.14 $3p(^3P)3d\,^4S$	$+0.09$ $(^3P)3p\,^4P$
$^4D_{7/2}$	0.99 $(^3P)3p\,^4D$	-0.09 $3p(^3P)3d\,^4D$	
$^4D_{5/2}$	0.95 $(^3P)3p\,^4D$	$+0.16$ $(^3P)3p\,^4P$	-0.12 $(^1P)3p\,^2D$
$^4D_{3/2}$	0.95 $(^3P)3p\,^4D$	$+0.16$ $(^3P)3p\,^4P$	-0.12 $(^1P)3p\,^2D$
$^4D_{1/2}$	0.97 $(^3P)3p\,^4D$	$+0.12$ $(^3P)3p\,^4P$	-0.11 $(^1P)3p\,^2P$
$^4P_{5/2}$	0.94 $(^3P)3p\,^4P$	$+0.24$ $(^1P)3p\,^2D$	$+0.16$ $(^3P)3p\,^2D$
$^4P_{3/2}$	0.89 $(^3P)3p\,^4P$	$+0.29$ $(^1P)3p\,^2D$	$+0.19$ $(^3P)3p\,^2D$
		-0.15 $(^1P)3p\,^2P$	-0.11 $(^3P)3p\,^2P$
$^4P_{1/2}$	0.97 $(^3P)3p\,^4P$	-0.13 $(^3P)3p\,^4D$	-0.10 $(^1P)3p\,^2S$
		Mg II	
$^4S_{3/2}$	0.99 $(^3P)3p\,^4S$	-0.12 $3p(^3P)3d\,^4S$	
$^4D_{7/2}$	0.99 $(^3P)3p\,^4D$		
$^4D_{5/2}$	0.97 $(^3P)3p\,^4D$	$+0.14$ $(^3P)3p\,^4P$	-0.12 $(^1P)3p\,^2D$
$^4D_{3/2}$	0.96 $(^3P)3p\,^4D$	$+0.15$ $(^3P)3p\,^4P$	-0.13 $(^1P)3p\,^2D$
$^4D_{1/2}$	0.98 $(^3P)3p\,^4D$	$+0.10$ $(^3P)3p\,^4P$	-0.11 $(^1P)3p\,^2P$
$^4P_{5/2}$	0.95 $(^3P)3p\,^4P$	$+0.23$ $(^1P)3p\,^2D$	$+0.15$ $(^3P)3p\,^2D$
$^4P_{3/2}$	0.90 $(^3P)3p\,^4P$	$+0.28$ $(^1P)3p\,^2D$	$+0.18$ $(^3P)3p\,^2D$
		-0.15 $(^1P)3p\,^2P$	-0.11 $(^3P)3p\,^2P$
$^4P_{1/2}$	0.98 $(^3P)2p\,^4P$	-0.11 $(^3P)3p\,^4D$	-0.11 $(^1P)3p\,^2S$

fact used. These were obtained by combining, for example,

$$c_1(^3P)3p_1\,^4L + c_2(^3P)4p_1\,^4L$$

to yield

$$c(^3P)3p\,^4L \quad \text{where } c^2 = c_1^2 + c_2^2 \,.$$

For the even $2p^5 3s 3p$ quartets, Table III shows there is marginally more mixing of terms and configurations in Na I than in Mg II. Generally, the spin-orbit mixing of different terms of the same configuration is greater than the correlation mixing of different configuration with the same term value. The configuration contributing the most to the latter category is the $2p^5 3p 3d$ configuration, though its composition is appreciable only in the $^4S_{3/2}$ and $^4D_{7/2}$ states.

For the $2p^5 3s 3d$ quartets, the mixing of the different terms of this configuration is seen in Table IV to be somewhat less in Mg II than in Na I. On the other hand, the

TABLE IV. Composition of $2p^5 3s 3d$ quartet states in Na I and Mg II (in order of energy).

Term		Wave-function expansion	
		Na I	
$^4P_{1/2}$	$0.97\ (^3P)3d\,^4P$	$+0.20\ (^3P)3d\,^4D$	$-0.10\ 3p(^3P)4f\,^4P$
$^4P_{3/2}$	$0.76\ (^3P)3d\,^4P$	$-0.38\ (^3P)4s\,^2P$	$+0.34\ (^3P)3d\,^4D$
		$+0.31\ (^1P)4s\,^2P$	
	$[0.88\ (^3P)3d\,^4P$	$+0.44\ (^3P)3d\,^4D]$[a]	
$^4F_{9/2}$	$0.99\ (^3P)3d\,^4F$		
$^4P_{5/2}$	$0.67\ (^3P)3d\,^4P$	$+0.66\ (^3P)3d\,^4D$	$+0.30\ (^3P)3d\,^4F$
$^4F_{7/2}$	$0.74\ (^3P)3d\,^4F$	$+0.65\ (^3P)3d\,^4D$	
$^4F_{5/2}$	$0.76\ (^3P)3d\,^4F$	$-0.55\ (^3P)3d\,^4P$	$+0.22\ (^3P)3d\,^4D$
		$-\ 0.18\ (^1P)3d\,^2D$	
$^4D_{3/2}$	$0.66\ (^3P)3d\,^4D$	$+0.59\ (^3P)3d\,^4F$	$+0.36\ (^3P)3d\,^4P$
		$-0.15\ (^1P)3d\,^2D$	$-0.14\ (^1P)3d\,^2P$
$^4D_{7/2}$	$0.73\ (^3P)3d\,^4D$	$-0.63\ (^3P)3d\,^4F$	$+0.21\ (^1P)3d\,^2F$
$^4D_{1/2}$	$0.93\ (^3P)3d\,^4D$	$-0.22\ (^1P)3d\,^2P$	$-0.18\ (^3P)3d\,^4P$
$^4D_{5/2}$	$0.69\ (^3P)3d\,^4D$	$-0.52\ (^3P)3d\,^4F$	$-0.43\ (^3P)3d\,^4P$
		$+0.17\ (^1P)3d\,^2F$	
$^4F_{3/2}$	$0.76\ (^3P)3d\,^4F$	$-0.56\ (^3P)3d\,^4D$	$+0.19\ (^3P)3d\,^4P$
		$+0.14\ (^1P)3d\,^2P$	$-0.11\ (^1P)3d\,^2D$
		Mg II	
$^4P_{1/2}$	$0.91\ (^3P)3d\,^4P$	$-0.34\ (^3P)4s\,^4P$	$-0.18\ 3p^2(^3P)\,^4P$
		$+0.10\ (^3P)3d\,^4D$	$-0.10\ 3p(^3D)4f\,^4P$
$^4P_{3/2}$	$0.76\ (^3P)3d\,^4P$	$-0.52\ (^3P)4s\,^4P$	$+0.21\ (^3P)3d\,^4D$
		$-0.16\ 3p^2(^3P)\,^4D$	$-0.16\ (^3P)4s\,^2P$
			$-0.10\ (^1P)4s\,^2P$
	$[0.81\ (^3P)3d\,^4P$	$+0.54\ (^3P)4s\,^4P$	$+0.20\ (^3P)3d\,^4D$
		$-0.11\ 3p^2(^3P)\,^4P$	$-0.15\ (^3P)4s\,^2P$
			$+0.10\ 3p^2(^3P)\,^4D]$[a]
$^4F_{9/2}$	$0.99\ (^3P)3d\,^4F$		
$^4P_{5/2}$	$0.87\ (^3P)3d\,^4P$	$+0.36\ (^3P)3d\,^4D$	$+0.19\ (^3P)4s\,^4P$
		$+0.15\ 3p^2(^3P)\,^4D$	$+0.13\ (^3P)3d\,^4F$
		$-0.11\ 3p^2(^3P)\,^4P$	
$^4F_{7/2}$	$0.92\ (^3P)3d\,^4F$	$+0.35\ (^3P)3d\,^4D$	$-0.10\ (^1P)3d\,^2F$
$^4F_{5/2}$	$0.89\ (^3P)3d\,^4F$	$+0.30\ (^3P)3d\,^4D$	$-0.24\ (^3P)3d\,^4P$
		$-0.13\ (^1P)3d\,^2D$	$-0.12\ (^1P)3d\,^2F$
$^4F_{3/2}$	$0.85\ (^3P)3d\,^4F$	$+0.43\ (^3P)3d\,^4D$	$-0.17\ (^1P)3d\,^2D$
		$-0.11\ (^3P)3d\,^4P$	
$^4D_{7/2}$	$0.90\ (^3P)3d\,^4D$	$-0.31\ (^3P)3d\,^4F$	$+0.23\ (^1P)3d\,^2F$
		$+0.14\ (^3P)3d\,^2F$	
$^4D_{1/2}$	$0.91\ (^3P)3d\,^4D$	$-0.25\ (^1P)3d\,^2P$	$-0.17\ (^3P)3d\,^2P$
		$+0.14\ 3p^2(^3P)\,^4D$	$+0.10\ (^3P)4s\,^2P$
$^4D_{3/2}$	$0.65\ (^3P)3d\,^4D$	$+0.55\ (^3P)4s\,^2P$	$-0.37\ (^3P)3d\,^4F$
		$-0.20\ (^1P)3d\,^2P$	$+0.16\ (^3P)4s\,^4P$
		$+0.13\ (^1P)4s\,^2P$	$-0.11\ (^3P)3d\,^2P$
		$-0.10\ (^3P)3d\,^4P$	
$^4D_{5/2}$	$0.83\ (^3P)3d\,^4D$	$-0.33\ (^3P)3d\,^4F$	$-0.28\ (^3P)3d\,^4P$
		$+0.23\ (^1P)3d\,^2F$	$+0.14\ (^3P)3d\,^2F$
		$-0.10\ (^1P)3d\,^2D$	

[a] Expansion using basis for $3s\ (^3P)4s\,^4P$.

TABLE V. Composition of $2p^53s4s$ states of Na I and Mg II.

Term		Wave-function expansion	
		Na I	
$^4P_{5/2}$	0.99 $(^3P)4s\,^4P$	$+0.11$ $3p(^3D)4p\,^4P$	
$^4P_{3/2}$	0.94 $(^3P)4s\,^4P$	-0.26 $(^3P)4s\,^2P$	-0.18 $(^1P)4s\,^2P$
		$+0.10$ $3p(^3D)4p\,^4P$	
$^4P_{1/2}$	0.94 $(^3P)4s\,^4P$	-0.24 $(^3P)4s\,^2P$	-0.20 $(^1P)4s\,^2P$
		$+0.10$ $3p(^3D)4p\,^4P$	
		Mg II	
$^4P_{5/2}$	0.97 $(^3P)4s\,^4P$	-0.18 $(^3P)3d\,^4P$	$+0.10$ $3p(^3D)4p\,^4P$
$^4P_{3/2}$	0.80 $(^3P)4s\,^4P$	-0.51 $(^3P)3d\,^4P$	-0.18 $(^3P)4s\,^2P$
		-0.11 $(^3P)3d\,^4D$	-0.12 $(^1P)4s\,^2P$
$^4P_{1/2}$	0.86 $(^3P)4s\,^4P$	-0.37 $(^3P)3d\,^4D$	-0.22 $(^3P)4s\,^2P$
		-0.20 $(^1P)4s\,^2P$	$+0.10$ $3p(^3D)4p\,^4P$

nonrelativistic Coulomb interaction with $2p^53s4s$ and also $2p^53p^2(^3P)$ is more pronounced in Mg II. Two expansions are given for the $2p^53s3d\,^4P_{3/2}$ state. The first was obtained using the basis for $(^3P)3d\,^4P$, the second using the basis for $(^3P)4s\,^4P$. In Mg II there is not a great deal of difference between the two expansions, but in Na I the difference is great. The mixing of $(^3P)3d\,^4P$ with $(^{1,3}P)4s\,^2P$ in Na I is *not* the result of a direct Coulomb interaction *nor* a spin-orbit interaction. In the $(^3P)3d\,^4P$ basis, the $4s$ and $5s$ orbitals are correlation orbitals for the ^4P state. As a result, the energies of the $(^{1,3}P)4s\,^2P$ configuration states are too high and close to $(^3P)3d\,^4P$. The large contribution to the wave function could then arise from the two-body magnetic operators, spin other orbit and spin spin. We believe the presence of the $(^{1,3}P)4s\,^2P$ components in the wave function are spurious. As a check, another calculation was performed in which the $4s$ orbital was determined by an MCHF calculation over the set of configuration states $2p^5\{3s(^3P)4s,\ 3s(^1P)4s,\ 3s^2\}\,^2P$, with dominant component $(^3P)4s\,^2P$. With this basis the total energy of the $^4P_{3/2}$ state was raised by only 66 cm^{-1}, but the $(^{1,3}P)4s\,^2P$ components had essentially disappeared, having coefficients less than 0.05 in magnitude. The "best" basis is usually the one which yields the lowest total energy. For this reason, we will report these energies, but transition probabilities for the $(^3P)3d\,^4P_{3/2}$ state will be based on the *second* wave-function expansion.

For the $2p^53s4s$ quartet, term mixing with the $2p^53s4s$ doublet also is less in Mg II than in Na I, as seen in Table V. The greater importance of the Coulomb interaction between $(^3P)4s\,^4P$ and $(^3P)3d$ in Mg II is clearly evident.

For the $2p^53p^2(^3P)$ quartets in Mg II, term mixing is negligible, the most important interaction being the Coulomb interaction with $2p^53d^2(^3P)$. The latter was essentially independent of the final-term value and resulted in a wave-function expansion of

$$0.99\ 2p^53p^2(^3P)+0.12\ 2p^53d^2(^3P)$$

for Mg II, though the ^4P states also contained 0.12 $3s(^3P)3d$.

It is interesting to compare the mixings in Na I with those reported by Holmgren *et al.*[1] based on the semi-empirical multiconfiguration method. For the even quartets there is a similar mixing of terms, but in the present work the extent of the mixing is generally less. For the odd quartets, on the whole the dominant components and major contributors are all in agreement (the differences in sign are not significant, being due to differing phase conventions) but again, in general, the mixing of terms is somewhat less in the present calculations. The one exception is the first $J=5/2$ state, a highly mixed state. In the present work, the third $J=5/2$ state has more ^4D character than any other LS value, and so we have labeled it $^4D_{5/2}$. The second $J=5/2$ state is predominantly ^4F, and so, by default, we have labeled the first $J=5/2$ state as $^4P_{5/2}$. This order is also the order in which $J=5/2$ states occur in Mg II. Note the good agreement in the Holmgren *et al.* expansion of $2p^53s3d\,^4P_{3/2}$ with the second expansion in Table IV for this state.

IV. LIFETIME COMPUTATION

The decay mechanisms for the odd quartets can be classified into three categories: (i) radiative decay to $2p^6ns\,^2S$ or $2p^6nd\,^2D$ states, (ii) radiative decay to $2p^53s3p$ states, and (iii) autoionization. Transition rates for the second category can be determined directly from the wave-function expansions described in the preceding section. Such calculations have been performed using theoretical wavelengths.

With the exception of a few metastable states, the lifetimes of many states depend critically on autoionization rates. These have been estimated using the theory presented by Cowan.[2] In this theory the autoionization rate is proportional to the square of the Coulomb interaction between a bound perturber and a continuum function, namely $2p^6kp$ for $J=1/2$ or 3/2 and $2p^6kf$ for $J=5/2$ or 7/2. The kp and kf continuum orbitals were computed within the $1s^22s^22p^6$ core as defined by the $1s$, $2s$, and $2p$ orbitals obtained from the $2p^53s$ Hartree-Fock calculation: the kp orbital was required to be orthogonal to the $2p$ orbital. The energy of the continuum electron was defined as the energy of the bound state (perturber) minus the energy of the $2p^6$ core as determined by these orbitals. Had it been based on the Hartree-Fock energy of the $2p^6$ core, the energy of the continuum electron would have been somewhat greater, but more assumptions would have been needed to evaluate the Coulomb interaction matrix element. Even so, it was necessary to introduce some assumptions, assumptions more likely to affect autoionizing rates to the kp continuum than the kf continuum.

For example, the wave-function expansion for a bound $2p^53s3d$ state includes the $2p^53p_34f_3$ configuration state. Then, since kp is not orthogonal to $3p_3$, the expression for the interaction between this state and $2p^6kp$ may contain a term of the form

$$R^2(2p2p;2p4f_3)\langle kp\,|\,3p_3\rangle\ ,$$

where $R^2(2p2p;\,2p4f_3)$ is a Slater integral and $\langle kp\,|\,3p_3\rangle$ an overlap integral. In the present calculations it was assumed that such overlap integrals were zero, which is equivalent to assuming all orbitals are orthogonal when matrix elements are evaluated. Since configuration states with outer p orbitals play a relatively minor role in the wave function expansion for $2p^53s3d$ quartets, the assumption is not likely to lead to a great loss in accuracy. It is likely to be a bigger factor for the $2p^53p^2$ states.

Cowan's program makes similar assumptions. A major difference between his code and the present calculation is the fact that orbitals in his code are not required to be orthogonal (even to the core) and that the energy of the continuum electron is determined from the Hartree-Fock energy of the $2p^6$ core. Also, the $2p$ orbitals of the bound and continuum states are allowed to differ.

Radiative decay rates to the $2p^6ns$ and $2p^6nd$ states are not as important to the lifetime prediction, but, for the sake of completeness, some simple calculations were performed. Only transitions to $2p^63s$ and $2p^63d$ were considered. For bound-state transitions, the present codes can account for only a limited amount of nonorthogonality between the orbitals of the two states in a rigorous fashion. For this reason, the $2p$ orbital of $2p^6$ need to be constrained to be the same as for the excited, $2p^5$ configuration. But, in this case, it was a simple matter to model the core as $\{2p^6,\,2p^53p\}$ (^1S) in an MCHF calculation for each state. All nonorthogonality effects were then included in the evaluation of the dipole matrix element.

In the next section, the configurations $2p^63s$ and $2p^63d$ will be referred to as "ground" configurations, and $2p^53s3p$ as the "excited" configuration. The three decay rates will be denoted $\sum_g A_{ij}$, $\sum_e A_{ij}$, and A, respectively.

V. RESULTS FOR Na I

The energy-level structure of the $2p^53s3p$ configuration is presented in Table VI and of $2p^53s3d$ and $2p^53s4s$ in Table VII. A number of core-excited quartet states have already been identified (see Holmgren *et al.*[1] for a brief historical review). These energy levels have been included in the tables for comparison. What is immediately apparent is that, within a term, the difference between observation and theory is essentially constant. This implies that our calculations have been successful at predicting

TABLE VI. Energy levels (in cm^{-1}) for $2p^53s3p$ states of Na relative to $2p^53s3p\,^4S_{3/2}$ ($E=-160.911\,983$ a.u.).

			Energy		
Configuration	Term	J	Theory	Obs.[a]	Theory − Obs.
$2p^53s(^3P)3p$	^4D	7/2	2726	2841	115
		5/2	3084	3187	103
		3/2	3434	3536	102
		1/2	3726	3830	104
	^4P	5/2	4795	4768	−27
		3/2	5179	5152	−27
		1/2	5381		
$2p^53s(^1P)3p$	^2D	3/2	5932		
		5/2	6389		
	^2P	1/2	6849		
		3/2	7138		
	^2S	1/2	9821		
$2p^53s(^3P)3p$	^2D	5/2	17 369		
	^2S	1/2	17 459		
	^2P	3/2	17 659		
	^2D	3/2	18 780		
	^2P	1/2	18 953		
$2p^53s(^3P)4s$	^4P	5/2	22 611	22 555	−56

[a] Holmgren *et al.* (Ref. 1).

the fine-structure splitting, but were not as successful in predicting the term energy separations. These tables include energies for the doublets, but it should be stressed that the main focus of this work has been the quartets; the calculations for the higher doublets are not expected to achieve the same degree of accuracy.

It is interesting to note that, in Na I, the $2p^53s(^3P)3d\,^2L$ terms are *lower* in energy than the corresponding quartet levels. This can be attributed, at least in part, to the interaction with the $2p^53p^2(^1D)\,^2L$ configuration. This is the analogue of the situation in Mg I where $3s3d\,^1D$ is lower than $3s3d\,^3D$.

Also included in Table VII are the autoionization rates. Of interest are levels for which the autoionization rate is less than 10^{10} sec^{-1}. This condition immediately excludes the low-lying doublets, with the possible exception of $2p^53s(^3P)3d\,^2D_{5/2}$. In their paper, Holmgren *et al.*[1] propose a laser based on $2p^53s(^1P)3d\,^2D_{5/2}$. Their calculations had predicted a transfer wavelength of 3140 Å, but they had not been able to observe fluorescence at that wavelength. The present calculations suggest that this level has a high autoionization rate.

In Table VIII, decay rates for selected levels in Na I are presented in units of 10^8 sec^{-1}, for the three modes of decay discussed in the preceding section. These data define the present lifetime, τ, also tabulated. The radiative decay rates to the excited $2p^53s\,3p$ levels are essentially the same for all terms of a configuration, but are smaller for $(^3P)4s$

TABLE VII. Energy levels (in cm^{-1}) for $2p^53s4s$ and $2p^53s3d$ states of Na relative to $2p^53s4s\,^4P_{5/2}$ (energy equals $-160.808\,96$ a.u.) and autoionization rates A in sec^{-1}.

				Energy		
Configuration	Term	J	Theory	Obs.[a]	Theory − Obs.	A
$2p^53s(^3P)4s$	^4P	5/2	0			8.5(−2)
		3/2	566			2.9(9)
		1/2	1102			3.9(8)
	^2P	3/2	2163			2.5(11)
		1/2	2367			2.9(10)
$2p^53s(^3P)3d$	^2P	1/2	3568			4.2(12)
	^2F	7/2	3706			3.8(10)
	^2P	3/2	3881			3.3(12)
	^2F	5/2	4220			1.6(10)
$2p^53s(^1P)4s$	^2P	3/2	4586			5.2(10)
		1/2	5213			3.4(11)
$2p^53s(^3P)3d$	^2D	5/2	5198			5.6(9)
		3/2	5354			8.5(11)
	^4P	1/2	5651	5919	(268)	2.1(8)
		3/2	5720	5988	(268)	3.2(10)
	^4F	9/2	5775	6040	(265)	0.0
	^4P	5/2	5839	6099	(260)	1.2(7)
	^4F	7/2	5887	6148	(261)	5.0(8)
		5/2	6348	6613	(265)	4.7(9)
	^4D	3/2	6447	6709	(262)	1.8(8)
		7/2	6466			2.3(10)
		1/2	6550			3.1(8)
		5/2	6945			1.5(10)
	$^4\mathrm{F}$	3/2	6957			6.6(9)
$2p^53s(^1P)3d$	^2F	5/2	8847			3.1(11)
	^2P	3/2	8899			1.0(8)
	^2F	7/2	9128			3.1(11)
	^2P	1/2	9132			1.2(8)
	^2D	3/2	9308			6.0(8)
		5/2	9344			2.0(10)

[a] Holmgren *et al.* (Ref. 1).

TABLE VIII. Transition rate data ($\sum_g A_{ij}$, transitions to $2p^63s$ or $2p^63d$; $\sum_e A_{ij}$, transitions to $2p^53s3p$; A, autoionization rate), in units of 10^8 sec^{-1}, and lifetimes, in nsec, for selected levels in Na I.

Term	J	$\sum_g A_{ij}$	$\sum_e A_{ij}$	A	τ_{present}	τ_{other}[a]	τ_{expt}[b]
$(^3P)4s\,^4P$	5/2	0.0	1.21	0.00	8.3	10.9	4.4±0.4
	3/2	0.75	1.20	28.7	0.32		
	1/2	0.80	1.21	3.9	1.7		
$(^3P)3d\,^2D$	5/2	0.18	0.32	56.2	0.18		
$(^3P)3d\,^4P$	1/2	0.01	2.02	2.12	2.4	5.8	2.95±0.20
	3/2	0.03	1.91	0.25	4.6	2.8	4.10±0.40
	5/2	0.03	1.96	0.12	4.7	6.1	3.34±0.20
^4F	9/2	0.00	1.97	0.00	5.1	6.1	4.38±0.20
	7/2	0.03	1.93	4.99	1.4	2.9	0.94±0.15
	5/2	1.25	1.95	46.7	0.20	0.18	0.40±0.20
	3/2	0.89	1.90	66.0	0.15		
^4D	7/2		1.90	226	0.04		
	5/2		1.91	150	0.065		
	3/2	1.22	1.90	1.80	2.0	0.48	0.70±0.07
	1/2	1.01	1.85	3.13	1.7		

[a] Holmgren *et al.* (Ref. 1) with $^4D_{5/2}$ reassigned to $^4P_{5/2}$.

[b] Engström *et al.* (Ref. 3) with $^4D_{5/2}$ reassigned to $^4P_{5/2}$.

than $(^3P)3d$. Most variable is the autoionization rate, followed by radiative decay to the $2p^6nl$ "ground" configurations.

The lifetimes predicted by the present calculations are compared with the theoretical values derived from Holmgren *et al.*[1] data and the experimental values of Engström *et al.*[3] For $(^3P)4s\,^4P_{5/2}$ state, which is metastable against autoionization as well as radiative decay to $2p^6nl$ doublets, the lifetime has been reduced slightly in the present work, but still differs almost by a factor of 2 from the experimental value. For all the $(^3P)3d\,^4P$ levels, the present lifetimes are in closer agreement with experiment: the present autoionization rates are larger for $J=1/2$ and 5/2 (previously labeled $^4D_{5/2}$) and smaller for $J=3/2$. The $^4F_{9/2}$ level can only decay to the $(^3P)3p\,^4D_{7/2}$ level. The smaller lifetime in better (but not excellent) agreement with experiment must be attributed to more reliable wave-function expansions. The lifetime for the $(^3P)3d\,^4F_{7/2}$ level is in better agreement due to a larger autoionization rate: the $^4F_{5/2}$ level has a shorter lifetime, essentially the same as the previously predicted lifetime. Only for the $^4D_{3/2}$ level is the radiative decay rate comparable in magnitude to the autoionization rate. The present lifetime is too long suggesting that decay to levels other than $2p^63d$ may be significant or that the autoionization rate is too small.

VI. RESULTS FOR Mg II

Energy levels for the $2p^53s3p$ configuration are reported in Table IX, whereas energy levels and autoionization rates are reported in Table X for the $2p^53s4s$ and $2p^53p^2$ configurations and the $2p^53s3d$ quartets (for $2p^53p^2$ the high-lying doublets are omitted). In Mg II, the $2p^53s3d$ quartets are all lower in energy than the doublets of this configuration. The $2p^53p^2(^1D)\,^2L$ terms are now lower in energy than the $2p^53s4s$ terms. Very little term mixing was observed for the $2p^53p^2(^3P)$ states. In particular, the ^2D and ^2S states, which are metastable against autoionization, are essentially free of autoionizing components. Ex-

TABLE IX. Theoretical energy levels (in cm^{-1}) for core-excited states of Mg II relative to $2p^53s(^3P)3p\,^4S_{3/2}$ ($E=-197.763\,90$ a.u.).

Configuration	Term	J	Energy (cm^{-1})
$2p^53s(^3P)3p$	^4D	7/2	4943
		5/2	5513
		3/2	6075
		1/2	6542
	^4P	5/2	8661
		3/2	9266
		1/2	9600
$2p^53s(^1P)3p$	^2D	3/5	10 457
		5/2	11 232
	^2P	1/2	12 002
		3/2	12 487
	^2S	1/2	17 071
$2p^53s(^3P)3p$	^2D	5/2	29 615
	^2P	3/2	30 543
		1/2	31 510
	^2D	3/2	32 176
	^2S	1/2	33 436
$2p^53s(^3P)4s$	^4P	5/2	58 607

TABLE X. Energy levels (in cm^{-1}) for $2p^5 3s 4s$ and $2p^5 3s 3d$ states of Mg II relative to $2p^5 3s 4s\,{}^4P_{5/2}$ (energy equals −197.496 86 a.u.) and autoionization rates A in sec^{-1}.

Configuration	Term	J	Energy	A	Configuration	Term	J	Energy	A
$2p^5 3s(^3S)4s$	^4P	5/2	0	5.7(5)		^2D	3/2	2070	7.0(7)
		3/2	792	5.4(9)			5/2	2731	7.9(6)
		1/2	2028	4.9(8)					
						^4S	3/2	4586	8.7(7)
$2p^5 3s(^1S)4s$	^2P	3/2	3941	1.2(11)		^2S	1/2	4586	5.9(7)
		1/2	4116	1.0(11)					
						^2P	1/2	8837	8.7(12)
$2p^5 3s(^1S)4s$	^2P	3/2	7618	4.1(12)			3/2	9215	8.7(12)
		1/2	8782	2.4(12)					
					$2p^5 3p^2(^1S)$	^2P	3/2	19 035	3.9(12)
$2p^5 3p^2(^1D)$	^2P	1/2	−10 312	1.1(13)			1/2	21 424	1.6(10)
		3/2	−9371	1.1(13)					
	^2F	7/2	−9328	9.9(10)	$2p^5 3s(^3P)3d$	^4P	1/2	981	4.8(9)
		5/2	−7713	9.2(10)			3/2	1539	6.6(9)
	^2D	5/2	−5824	8.0(10)			5/2	1801	3.1(6)
		3/2	−5273	1.2(9)					
						^4F	9/2	1675	0.0
$2p^5 3p^2(^3P)$	^4P	5/2	−3809	3.4(3)			7/2	2073	1.1(10)
		3/2	−3243	6.1(7)			5/2	2578	1.8(10)
		1/2	−2898	6.5(7)			3/2	3003	2.5(10)
	^4D	7/2	−1423	2.1(7)		^4D	7/2	3347	6.0(10)
		5/2	16	6.6(6)			5/2	3978	6.1(10)
		3/2	594	6.4(7)			3/2	3944	2.3(11)
		1/2	941	1.7(8)			1/2	3671	3.0(11)

TABLE XI. Transition rate data ($\sum_g A_{ij}$, transitions to $2p^6 3s$ or $2p^6 3d$; $\sum_e A_{ij}$, transitions to $2p^5 3s\,3p$; A, autoionization rate) in units of 10^8 sec^{-1}, and lifetimes, in nsec, for selected levels of Mg II.

Term	J	$\sum_g A_{ij}$	$\sum_e A_{ij}$	A	τ
$3p^2(^1D)\,^2D$	5/2	3.33	0.10	12.0	0.612
$3p^2(^3P)\,^4P$	5/2	0.003	11.10	0.00	0.901
	3/2	0.004	11.21	0.61	0.846
	1/2	0.002	11.30	0.65	0.837
$3s(^3P)4s\,^4P$	5/2	0.02	7.81	0.006	1.28
	3/2	1.12	8.47	54.2	0.157
	1/2	3.94	8.62	4.87	0.574
$3s(^3P)3d\,^4P$	1/2	0.04	10.35	48.3	0.170
	3/2	2.96	10.41	66.0	0.126
	5/2	0.51	11.10	0.03	0.859
$3s(^3P)3d\,^4F$	9/2	0.0	11.32	0.0	0.883
$3p^2(^3P)\,^4D$	7/2	0.002	11.55	0.21	0.851
	5/2	0.000	11.60	0.07	0.857
	3/2	0.008	11.51	0.64	0.822
	1/2	0.021	11.56	1.72	0.752
^2D	5.2	0.80	10.50	0.08	0.945
	3/2	0.79	10.46	0.70	0.837
^4S	3/2	0.017	12.59	0.87	0.742
^2S	1/2	0.001	10.85	0.59	0.874

perimental results are not available for comparison.

Transition rate data and predicted lifetimes are reported in Table XI for selected levels of Mg II. The majority of levels are for the $2p^5 3p^2(^3P)$ configuration. What is immediately apparent is the relatively small autoionization rate. It is also clear that the lifetimes of these levels are determined primarily by decay to the $2p^5 3s 3p$ levels ($\sum_e A_{ij}$) for which the decay rate is relatively constant. Only a few of the $(^3P)4s$ or $(^3P)3d$ quartet levels have lifetimes greater than 0.1 nsec. These include the $(^3P)4s\,^4P_{5/2}$, $(^3P)3d\,^4P_{5/2}$, and $(^3P)\,^4F_{9/2}$ levels which were metastable against autoionization also in Na I.

VII. CONCLUSION

Theoretical lifetimes have been predicted for some of the odd quartet levels in Na I and Mg II. Levels of interest in the construction of xuv lasers are those with large radiative decay modes both to "ground" configurations and to the metastable $2p^5 3s 3p\,^4S_{3/2}$ excited level. In Na I, the levels investigated for this purpose were $(^3P)3d\,^4D_{3/2}$ and $^4F_{5/2}$. In Mg II, the $(^3P)4s\,^4P_{1/2}$ and $(^3P)3d\,^4P_{3/2}$ have similar characteristics.

Calculations for core excited quartets are sensitive to the radial basis. By including term dependence, the $2p^5 3s 3p$ and $2p^5 3s 3d$ doublets were better represented and doublet-quartet mixing was reduced, at least for the larger components. The present calculations differ from Cowan's in that the Breit-Pauli operator includes more effects than just spin-orbit interaction. In particular, the spin-spin operator will mix configurations with no spin-orbit interaction between them. However, these differences are likely to be relatively minor. Of greater concern is the assumption that continuum orbitals are orthogonal to orbitals occupied in the bound perturber when, in fact, they are not orthogonal. A more rigorous computational procedure is needed, possibly one similar to the procedure recently described by Beck and Nicolaides.[13]

In the present study, large autoionization rates are used to *eliminate* levels from further consideration and in such circumstances, do not need to be known accurately. In some instances autoionization rates play an important role in the lifetime prediction and errors in these rates could be an explanation for discrepancy between theory and experiment. In Na I, however, the largest discrepancy is for the $(^3P)4s\,^4P_{5/2}$ level which is metastable against autoionization and decay to $2p^6 nl$ doublets. Experimental data for Mg II would be valuable for comparison purposes.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under Contract Nos. De-AS05-80ER10618 and W-31-109-Eng-38. The author wishes to acknowledge the encouragement given by G. Berry for pursuing this research as well as assistance and discussions with R. D. Cowan concerning autoionization calculations.

---

*On leave from Vanderbilt University, Box 6035B, Nashville, TN 37235.

[1] D. E. Holmgren, D. J. Walker, D. A. King, and S. E. Harris, Phys. Rev. A **31**, 677 (1985).

[2] R. D. Cowan, *The Theory of Atomic Structure and Spectra* (University of California, Berkeley, 1981).

[3] L. Engström, L. Young, L. P. Somerville, and H. G. Berry, Phys. Rev. A **32**, 1468 (1985).

[4] C. Froese Fischer, Can. J. Phys. **53**, 184 (1975); **53**, 338 (1975).

[5] C. Froese Fischer, J. Phys. B **16**, 157 (1983).

[6] C. Froese Fischer, *The Hartree-Fock Method for Atoms* (Wiley, New York, 1977).

[7] J. P. Desclaux, Comput. Phys. Commun. **9**, 31 (1971).

[8] I. P. Grant, B. J. McKenzie, P. H. Norrington, D. F. Mayers, and N. C. Pyper, Comput. Phys. Commun. **21**, 207 (1980).

[9] K. N. Huang, Y. K. Kim, and K. T. Cheng, Phys. Rev. Lett. **48**, 1245 (1982).

[10] R. Glass and A. Hilbert, Comput. Phys. Commun. **16**, 19 (1978).

[11] A. Hibbert, R. Glass, and C. Froese Fischer (unpublished).

[12] H. G. Berry, R. Hallin, R. Sjödin, and M. Gaillard, Phys. Lett. **50A**, 191 (1974).

[13] R. Beck and C. A. Nicolaides, Proceedings of the Workshop on Some Aspects of Autoionization in Atoms and Small Molecules, Argonne National Laboratory Report No. ANL-PHY-85-3, Argonne, IL, 1985 (unpublished).