Effects of Core-valence and Core-core Correlation On the Line-strength of the Resonance Lines In Li-i and Na-i

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Effects of core-valence and core-core correlation on the line strength of the resonance lines in Li I and Na I

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The resonance lines in Li I and Na I both exhibit a puzzling discrepancy between experiment and accurate *ab initio* calculations. Only results from a semiempirical method, that in principal neglects core-core correlation, agree with the experiments. The agreement with a multiconfiguration Hartree-Fock calculation, including only core-valence correlation, shows that this might be fortuitous. A method for including some core-core correlation is designed and gives results in excellent agreement with other accurate *ab initio* methods.

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The resonance lines in Li I ($2s\,^2S-2p\,^2P$) and Na I ($3s\,^2S-3p\,^2P$) have recently attracted a great deal of interest [1–3] due to a seemingly persistent discrepancy between *ab initio* theoretical and experimental line strengths. A semiempirical method [1], based on the Coulomb approximation with a Hartree-Slater core (CAHS), on the other hand, reproduces the most accurate experimental values perfectly. The conclusion has been made that this approach yields "transition rates superior to those obtained by fully *ab initio* methods." In this report we will show that it is possible to produce results in agreement with experiment, even with *ab initio* methods, by including only core polarization contributions to the line strength. We will argue that the main difference between the semiempirical results reported by Theodosiou, Curtis, and El-Mekki and the *ab initio* ones lies in the type of correlation included in the calculations.

Let us start by investigating lithium, keeping in mind that we ultimately are interested in more complex systems. The light lithium atom presents an experiment with quite a challenge, while this three-electron system can be treated very accurately by a number of different theories. The most accurate experimental results, judging from the error bars, is the beam-laser one by Gaupp, Kuske, and Andrä [4]. The delayed-coincidence experiment by Carlsson and Sturesson [5] gives a somewhat larger line strength, and the larger error bars overlap with most theoretical results. On the theoretical side a large number of very accurate *ab initio* methods have been applied. Most recently Blundell *et al.* [6] used relativistic many-body perturbation theory (MBPT), while Mårtensson-Pendrill and Ynnerman [7] applied the coupled-clouster approach including single and double excitations (CCSD), Pipin and Bishop [8] performed Hylleraas types of calculations, Weiss [9] did large-scale configuration interaction (CI), Chung [10] used a full-core plus correlation (FCPC) method, and Tong, Jönsson, and Fischer [11] reported on multiconfiguration Hartree-Fock (MCHF) calculations. All these methods, though quite different, are in perfect agreement (see Table I), but give a line strength significantly larger than the experimental one by Gaupp, Kuske, and Andrä. Only the semiempirical calculations by Theodosiou, Curtis, and El-Mekki [1] support this experiment.

The lithium atom is a system with one electron outside closed subshells, and consequently there is no outer correlation. The corrections to the Hartree-Fock results can therefore be classified as either core-valence or core-core correlations. All the *ab initio* methods cited here include both these types of corrections. For the semiempirical method used by Theodosiou, Curtis, and El-Mekki it is not clear what type of correlation is included implicitly through the fitting procedures to experimental energies, but explicitly only core polarization is included. Therefore, our first task will be to investigate the importance of core-core contributions to the line strength.

Our method of choice is the *ab initio* MCHF active set approach. The basic ideas for this approach have been described elsewhere [12], so let us here only summarize some important concepts for the present case. In an MCHF calculation, the atomic state function is represented by a linear combination of configuration state functions (CSF's),

$$\Psi(\gamma LS)=\sum_{i=1}^{M} c_i\Phi(\gamma_i LS)\ . \tag{1}$$

The CSF's are generated by excitations from the reference configuration to the active set of orbitals. By restricting the way excitations can be done, different correlation effects can be studied. The size of the active set determines to what accuracy these correlation effects are represented in the wave function.

To treat core-valence correlation (or core polarization) in lithium, we include all CSF's of the form,

$$1s^2nl \quad \text{and} \quad 1sn'l'n''l''\ . \tag{2}$$

We will label this approach, which only includes core polarization, MCHF-CP. The results from calculations for active sets with $n_{\max}$ up to 7 are given in Fig. 1. The resulting line strength converges to a value (32.7987 a.u.), in excellent agreement with the experimental value of Gaupp, Kuske, and Andrä [4] and the semiempirical results by Theodosiou, Curtis, and El-Mekki [1]. The latter is not surprising, since the two methods include similar effects.

TABLE I. Recent results for the line strength (in a.u.) of the resonance lines in Li I and Na I, arranged according to types of correlation included.

Method	Li I Ref.	Li I S	Na I Ref.	Na I S
		Core polarization only		
CAHS	[1]	32.74	[19]	37.05
CA			[20]	37.25
MP			[20]	37.20
MCHF-CP($2p$)[a]			Present	37.19
MCHF-CP	Present	32.80	Present	36.84
		Including Core-core		
MBPT	[6]	32.99	[17]	37.42
CCSD	[7]	33.00	[18]	37.56
Hylleraas	[8]	33.00		
CI	[9]	33.03		
FCPC	[10]	33.01		
MCHF	[11]	33.00		
MCHF-CCP	Present	33.01	Present	37.39
		Experiment		
Beam-Laser	[4]	32.76±0.05	[4]	37.04±0.08
			[13]	37.04±0.12
Laser Spectr.	[5]	32.85±0.24	[14]	37.09±0.18, 37.02±0.23[b]
			[15]	37.15±0.14[c]

[a]Including only $2p$ core polarization.
[b]Resuls for $J=\frac{1}{2}$ and $\frac{3}{2}$, respectively.
[c]Results for $J=\frac{1}{2}$.

For lithium it is possible to perform full correlation calculations by including all CSF's that can be generated from the active set and are of the completely unrestricted form,

$$nln'l'n''l'' \ . \tag{3}$$

This approach was used and driven to convergence by Tong, Jönsson, and Fischer [11]. The difference between their results and the MCHF-CP ones is a measure of the importance of the core-core correlation. With a maximum n quantum number of 7 this gave a line strength of 33.0152 a.u. Since this is quite far from the MCHF-CP result, it is clear that the core-core effect is not negligible. This comparison shows that it is not enough, for lithium, to only include core polarization, and that the agreement with experiment for the MCHF-CP (and possibly the semiempirical method by Theodosiou, Curtis, and El-Mekki) is fortuitous.

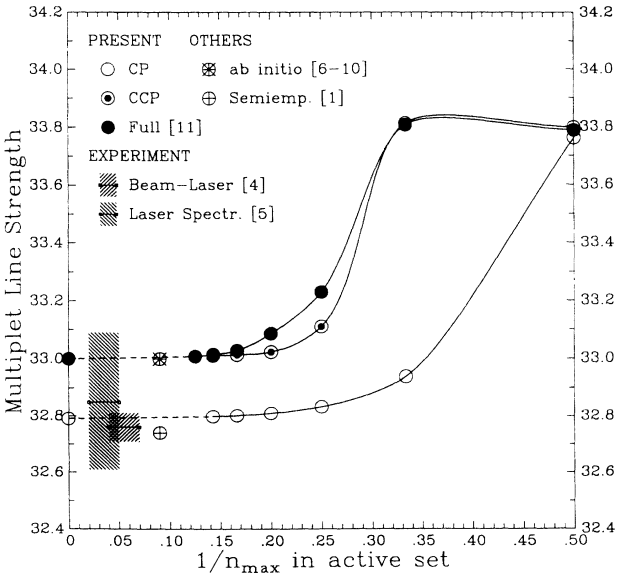

FIG. 1. Line strength (in a.u.) for the $2s\ ^2S-2p\ ^2P$ resonance line in Li I. CP = Core polarization only included. CCP stands for the approximate treatment of core-core correlation (see text). Full stands for the full correlation MCHF calculation by Tong, Jönsson, and Fischer [11].

The full-correlation approach used for lithium is not feasible for larger systems, such as sodium. We will therefore attempt to devise a simplified approach to include core-core correlation (or at least estimate the importance of it). We will label this method MCHF-CCP. There are two important properties of the full MCHF calculations of Tong, Jönsson, and Fischer that are hard to generalize. First, the fact that core-core correlation is included would, for sodium, give a fast growing number of CSF's as a function of the size of the active set. Second, all orbitals are separately optimized on the two states. For sodium we will need to keep, at least, the core orbitals common.

We base the MCHF-CCP approach on the observation that one of the most important contributions from the inclusion of core-core correlation is indirect, via the effect on the outer orbitals. We therefore will use a method that includes both core polarization and core-core correlation in the first few steps, and then concentrate on only the more important former effect. For lithium we start by obtaining a $1s$ orbital from a Hartree-Fock calculation on $1s^22s\ ^2S$. This is kept fixed for the rest of the calcula-

tions. Next, we perform full correlation calculations for active sets with $n_{max}=2$ and 3, i.e., we include all CSF's of the unrestricted form $nln'l'n''l''$. For larger active sets, the new CSF's included are of the form

$$1snln'l', \quad n,n' \leq 7 . \tag{4}$$

This implies that core-core correlation is represented only in the first two steps, and after that we concentrate on the core-valence correlation. The results are again given in Fig. 1, where we can see that the CCP results converge to the same line strength as the full correlation calculations (for $n_{max}=7$ the result is 33.0109 a.u.). As a matter of fact, the convergence seems to be faster for our limited core-core calculation. This is especially remarkable since the number of CSF's for $n_{max}=7$ is only 148 (248) for ^2S (^2P), compared to 1948 (4424) in the full correlation study.

To summarize our results for lithium, we have shown that core-core correlation gives important contributions to the line strength. An approach that includes only core polarization, such as MCHF-CP or the CAHS one by Theodosiou, Curtis, and El-Mekki, underestimates the line strength. We have also shown that the MCHF-CCP approach gives identical results to a full correlation calculation, as the one by Tong, Jönsson, and Fischer. Before moving on to sodium, we need to comment on the fact that we only report the length form of the line strength, as is common in most other methods. The velocity form will agree, to within a few tenths of a percent, with the length form for the full correlation study, but both in the MCHF-CP and MCHF-CCP calculations it deviates significantly and converges to a different value. The conclusion that MCHF-CCP reproduces the full correlation value is therefore only valid for the length form of the line strength.

The situation for sodium is very similar to the one for lithium. The most accurate experimental results, to date, are again from beam-laser measurements by Schmoranzer, Schulze-Hagenest, and Kandel [13] and Gaupp, Kuske, and Andrä [4]. The latter measured the lifetime of the $3p\ ^2P_{1/2}$ state with a 0.2% precision. Other results, from time-resolved laser spectroscopy [14,15] basically agree with these results, but have larger error bars. The value of Gaupp, Kuske, and Andrä has often been combined with an accurate measurement of the ratio of the line strength for the $\frac{1}{2}$ and $\frac{3}{2}$ states [16] to yield a value of the $3p\ ^2P_{3/2}$ state. This value, however, is not supported by any other measurement and is therefore not included in the tables or the future discussion of this report. The most accurate theoretical results are from MBPT, by Guet, Blundell, and Johnson [17], and CCSD, by Salomonson and Ynnerman [18]. It is clear, from Table I and Fig. 2, that the *ab initio* calculations give consistently larger line strengths than all experiments, while the semiempirical value by Theodosiou and Curtis [19], obtained by the same technique as for lithium, agrees perfectly with the experimental value of Gaupp, Kuske, and Andrä. Laughlin [20] performed similar Coulomb approximation (CA) and model-potential (MP) calculations, and obtained results in between the *ab initio* and experimental ones.

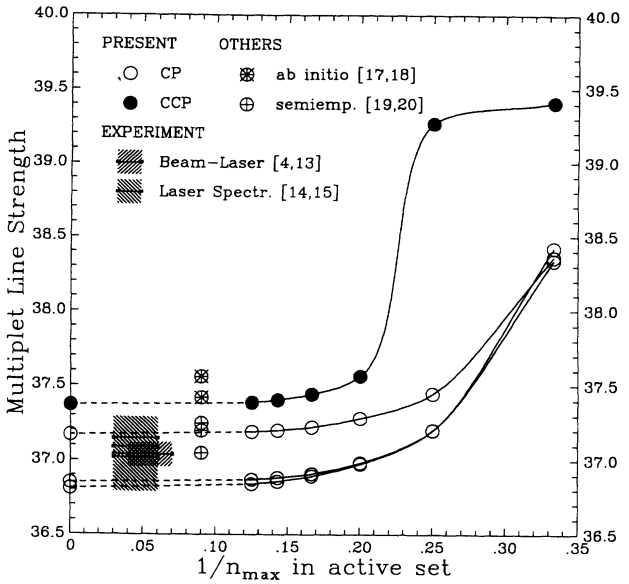

FIG. 2. Line strengths (in a.u.) for the $3s\ ^2S-3p^2P$ resonance line in a Na I for different approaches. CP stands for MCHF results, including core polarization; top curve with only polarization of the $2p$ subshell; second curve with also polarization of the $2s$ subshell; and third curve with polarization of the $1s$ subshell too. CCP stands for results including an approximate treatment of core-core correlation (see text).

We perform a number of different sets of MCHF calculations to investigate the importance of different effects. The MCHF-CP approach for sodium, with only core polarization included, involves three steps. The first, labeled CP($2p$), includes only polarization of the $2p$ subshell. This is done by including all CSF of the forms

$$1s^22s\ ^22p^6nl \quad \text{and} \quad 1s^22s\ ^22p^5n'l'n''l'' . \tag{5}$$

With $n_{max}=8$ this involves 290 (665) CSF's for the ^2S (^2P).

The second set, labeled CP($2s,2p$), includes also correlation between the $2s$ subshell and the outer $3s$ or $3p$ electron. This implies inclusion of CSF, in addition to the ones above, of the form

$$1s^22s2p^6nln'l' , \tag{6}$$

an approach that gives 453 and 939 CSF's for the two states involved, when $n_{max}=8$.

Finally, the polarization of the $1s$ subshell is also added, through inclusion of CSF of the form

$$1s2s^22p^6nln'l' , \tag{7}$$

in a calculation labeled CP($1s,2s,2p$). The final step, with $n_{max}=8$ involves in this case 616 and 1223 (CSF's).

The core orbitals ($1s$, $2s$, and $2p$) are obtained through a Hartree-Fock calculation on the ground state $3s\ ^2S$. We investigated the effect of choosing different cores, such as the one optimized on the excited $3p\ ^2P$ state, but the difference decreases when the active set increases and for $n_{max}=6$ was less than 0.02 a.u. in line strength.

The final MCHF-CCP set of calculations includes, in addition to the set of CSF's in the CP($1s,2s,2p$) calculations, also configurations of the type

$$1s^2 2s^2 2p^4 nln'l'n''l'' ,$$
$$1s^2 2s 2p^5 nln'l'n''l'' , \quad (8)$$
$$1s^2 2p^6 nln'l'n''l'' ,$$

but only for the first two steps in the active sets, that is, for $n_{max}=3$ and 4. We therefore include both core polarization and core-core correlation in the first two steps, and after that concentrate on the former. This is as close as possible to the MCHF-CCP calculation we performed for lithium. At least it should give a quite reliable estimate of core-core effects on the line strength. For $n_{max}=8$ the number of CSF's are for this approach 1017 and 2207, respectively, for the two terms under consideration. Due to limitations in the present version of the MCHF package, we also have to exclude some of the contributions to the transition matrix element, involving three overlaps. They are of the form

$$(c_i c_j' \text{ coefficient}) \times \langle 2s|E1|2p\rangle\langle nl|nl\rangle\langle n'l'|n'l'\rangle\langle n''l''|n''l''\rangle ,$$

which appear for transitions between states of the form,

$$2s^2 2p^4 nln'l'n''l'' \rightarrow 2s 2p^5 nln'l'n''l''$$

or

$$2s 2p^5 nln'l'n''l'' \rightarrow 2p^6 nln'l'n''l'' .$$

The product of the two weights $(c_i c_j')$ is less than 0.02 for all possible contributions, and the size of the $\langle 2s|E1|2p\rangle$ is about five "times" smaller than the $\langle 3s|E1|3p\rangle$ element. This leads immediately to a factor of 4×10^{-3} in the relative size of the contributions of this form, and the major contributions to the total matrix element. With the additional observation that the most important contributions come from matrix elements with the $3s$ occupied in the "lower" CSF, and $3p$ in the "upper," e.g., $\langle 2s^2 2p^4 3snp^2|E1|2s2p^5 3pn'sn''p\rangle$, we can conclude that the product of the three overlaps is small (<0.07). This is due to the fact that the outer $3s$ of the "lower" CSF is paired with an inner $n's$ of the upper, while the outer $3p$ and inner np are paired together. These overlaps are typically of the order 0.1–0.3, each. Only the $\langle np|n''p\rangle$ overlap is close to 1, in our example. This implies that the contribution from this type of matrix element is less than 0.03% of the total matrix element, which corresponds to a contribution of 0.02 to the line strength. A conservative estimate of the total contribution from these effects of 0.05 in line strength is of the same size as the error bars of the most accurate experiment and will not affect the conclusions in this report.

The results from all these calculations are given in Fig. 2. A number of interesting conclusions can be drawn from this. First, it is interesting to note that our MCHF-CP($2p$), which gives a line strength of 37.1936 a.u., and the CA-MP calculations by Laughlin agree very well, which is not surprising since they both only deal with polarization of the $2p$ core. Second, it is clear that $2s$ polarization is not negligible, and decreases the line strength by more than 0.3 a.u., to a value of 36.8715 a.u. for CP($2s,2p$). The effect of the $1s$ polarization is almost negligible, giving a line strength of 36.8414 a.u. for CP($1s,2s,2p$). More importantly, though, the core-core correlation counteracts the polarization of the two s subshells, and increases the line strength by almost 0.6 a.u. The final MCHF-CCP result is in excellent agreement with other *ab initio* theories. Just as for lithium we find that core-core correlation is not negligible and has to be included if one aims for anything more accurate than, say, 2–3 %.

To summarize our conclusions we can use Table I, where we show different results for line strengths from methods including different effects. It is clear that calculations including only core polarization underestimate the line strength, since the core-core correlation increases it significantly. The agreement with some experimental values of our MCHF-CP results and the semiempirical CAHS ones by Theodosiou, Curtis, and El-Mekki [1,19], both of which neglect the core-core correlation, cannot be explained.

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