I. INTRODUCTION

Given that a combined configuration-interaction (CI) and many-body-perturbation-theory (MBPT) approach could describe well experimental data for energies and transition rates in neon, it was a natural continuation to investigate a more difficult, stronger core-correlated atom such as argon. In argon theories and experiments appear to be less accurate than in neon, with larger mutual disagreement; moreover, heavier closed-shell atoms are even less studied and understood so that the argon atom can serve as an intermediate step in understanding many closed-shell atoms and ions.

Although semiempirical calculations \cite{1,2,3,4,5} sometimes lead to a good agreement with experiment for some transition arrays and provide valuable information for the analysis of existing experimental data, they do not explain much the nature of correlations and their predictive power is limited to cases where (a) energies are well-known and (b) energy-level information is sufficient to infer other atomic properties such as transition probabilities. In general two theories could give exactly the same energy levels without predicting the same transition probabilities. For example, adding or not adding random-phase approximation (RPA) corrections to transition amplitudes will give two different answers for transition rates although wave functions obtained from the same effective Hamiltonian are identical. When RPA corrections were included in neon \cite{6}, the improvement of agreement with experiment was only marginal and it was not an issue, but as we will show in this paper this type correction is crucial in argon. Hence, theories, which do not take into account at least the RPA correction, can be misleading in argon and heavier noble-gas atoms. Still owing to cancellations of RPA contributions for the same transition array, ratios obtained with a matrix method could be still accurate. Indeed, a fair agreement with experiment for low-lying argon transitions is obtained by Lilly \cite{7} even without considering RPA corrections. However, the accuracy of ratios decreases if relativistic and correlation effects, that introduce asymmetry for the \( p_{3/2} \) and \( p_{1/2} \) hole RPA contributions to radial transition integrals, are significant.

Another issue is the role of configuration interaction since many theories are limited by considering only a few configurations. The convergence of CI has to be investigated. Furthermore, other many-body effects, such as an interaction of a valence electron with a core or a hole with a core or their combination, are quite significant in argon and heavier noble-gas atoms. Thus, the development of \textit{ab initio} theory for heavy noble-gas atoms is needed to single out important correlation and relativistic effects. Some success is already achieved in this direction. For example, elaborate \textit{ab initio} calculations by Avgoustoglou and Beck \cite{8} performed for transitions from the lowest odd excited states \( 3p_{3/2}^{-1}4s_{1/2} \) and \( 3p_{1/2}^{-1}4s_{1/2} \) to the ground state give oscillator strengths in good agreement with average experimental values. However, this theory was not extended to transitions between excited states. Therefore, one objective of this paper is to prove that transitions between excited states of argon can also be calculated with \textit{ab initio} methods. We also would like to show that for argon our simpler CI+MBPT theory has comparable accuracy to complicated single-double couple-cluster (SDCC) method of Ref. \cite{9} and thus can be of practical value for other theoretical groups.

In this paper, first we will briefly describe our method of calculations (more details are given in \cite{10,11}); then, we will calculate energies and oscillator strengths of J=1 odd states and energies of J=2 even states and compare them with experiment. This comparison gives an estimate on accuracy of our wave functions. Next, we will present line strengths and rates for transitions between excited states and compare our result with experiment and semiempirical calculations.

II. CI+MBPT METHOD

We have developed a convergent variant of CI+MBPT for particle-hole states of closed-shell atoms \cite{5} and successfully applied it in neon to calculate energies \cite{8,6} and oscillator strengths for transitions between excited states \cite{8}. This perturbation theory is based on the first iteration of couple-cluster single-double equations \cite{10,11}. All second-order MBPT terms \cite{12} are included, with some denominators being modified to take into account the strong interaction between a hole and a core.

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Argon energies of J=1 odd and J=2 even states, oscillator strengths of the two lowest J=1 odd states, and line strengths for transitions between J=1 odd and J=2 even excited states are calculated with the CI+MBPT method. The results are in good agreement with experiment.

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electron or core and core electrons non-perurbatively. The advantage of this approach compared to the iterated single-double method is simplicity and speed of calculations. The accuracy of hole energies and fine-structure splittings is significantly improved already after adding second-order MBPT corrections as was illustrated previously in neon. Apart from Coulomb correlation corrections, the Breit magnetic interaction is also included, but small frequency-dependent Breit, quantum-electrodynamic, reduced-mass, and mass-polarization corrections are omitted.

To calculate particle-hole energies, we construct a model CI space, compute effective Hamiltonian in this space, and solve an eigenvalue problem. Along with energies we obtain wave functions, which are used to calculate transition amplitudes or other related quantities. We investigate energies, oscillator strengths for transitions to the ground state, and line strengths or transition rates for transitions between excited states. Energies of neon particle-hole J=1 odd states and oscillator strengths were in very good agreement with experiment: pure ab initio neon energies differed from experimental energies by 0.0069 a.u., but after subtraction of the systematic shift (which does not make much difference in transition calculations), the agreement was at the level of 0.0001 a.u. for almost all states. In this paper we use the same approach to calculate energies and transition amplitudes of argon.

Reduced matrix elements for transitions between particle-hole excited states are given in Ref. 8.

$$\langle F || Z_j || I \rangle = \sqrt{(2J_F + 1)(2J_I + 1)} \left\{ \begin{array}{l} (-1)^{J_J + J_a + J_v'} \left\{ \begin{array}{l} J_I \ J \ J_F' \\ J_J' \ J_a' \ J_v' \end{array} \right\} \delta_{a'a} \langle v' || Z_J || v \rangle + \\ (-1)^{J_F + J_a + J_v + 1} \left\{ \begin{array}{l} J \ J_F' \\ J_J' \ J_a' \ J_v \end{array} \right\} \delta_{v'v} \langle a || Z_J || a' \rangle \right\} $$

We found that second-order corrections to transition amplitudes or lowest order RPA corrections

$$Z_{ij}^{RPA} = Z_{ij} + \sum_{bm} \frac{Z_{bm} \tilde{g}_{jm} \tilde{Z}_{mb}}{\epsilon_b - \epsilon_m - \omega} + \sum_{bm} \frac{\tilde{g}_{bjm} Z_{mb}}{\epsilon_b - \epsilon_m + \omega} \quad (1)$$

are significant in argon. This type correction requires careful analysis since the possible interaction between an “observing” hole state a and core states b over which summation is carried out should be taken into account in all orders, at least a bulk part of this interaction. Similar to our approach for energies, we include the interaction in all orders by adding the extra term

$$extra = -\frac{X_0(abab)}{\sqrt{(2J_a + 1)(2J_b + 1)}} \quad (2)$$

in the denominators of RPA expressions. This procedure reduces RPA corrections roughly twice. If we note that the value of RPA correction is comparable to the values of lowest order matrix elements, the modification of the denominators is important and brings our theory to a good agreement with experiment which will be illustrated later in this paper.

### TABLE I: Energies of argon odd J=1 states

For unique specification of levels, accurate NIST energies are provided. The sizes of CI model spaces are denoted CI-22, etc. $\Delta_r$ is the deviation from experiment for the 7th level. All energies are expressed in atomic units

| State | NIST | CI-22 | CI-32 | CI-52 | $\Delta$ | $\Delta_r$ |
|-------|------|------|------|------|--------|----------|
| $p_3^1\, 3s$ | 0.4272 | 0.3202 | 0.4219 | 0.4219 | 0.0053 | 0.0129 |
| $p_3^1\, 4s$ | 0.4347 | 0.4291 | 0.4291 | 0.4297 | 0.0050 | 0.0126 |
| $p_3^1\, 5s$ | 0.5095 | 0.4925 | 0.4348 | 0.5083 | 0.0012 | 0.0088 |
| $p_3^1\, 5s$ | 0.5178 | 0.5082 | 0.5085 | 0.5250 | -0.0072 | 0.0004 |
| $p_3^1\, 6s$ | 0.5201 | 0.5234 | 0.5257 | 0.5268 | -0.0067 | 0.0009 |
| $p_1^1\, 5s$ | 0.5239 | 0.5268 | 0.5268 | 0.5317 | -0.0078 | -0.0002 |
| $p_1^1\, 6s$ | 0.5256 | 0.5331 | 0.5330 | 0.5332 | -0.0076 | 0.0000 |

### III. CALCULATIONS FOR ARGON

#### A. Energies of argon odd J=1 states

Table II shows our calculated energies for J=1 odd states. Fine structure for the 4s, 5s, or 4f groups of states is well reproduced since the deviation from experiment for each fine structure group of levels is similar. The last column shows shifted deviations from experiment, which demonstrate that there is a systematic shift for energy levels in our calculations. This shift is due to the inaccuracy of our calculations of hole energies. The shifted deviations illustrate a good precision for higher excited states which have smaller correlation effects. We also show the convergence with the number of particle-hole configurations. The change in energy is significant when we increase the size of CI space from 22 to 32 and to 52; however, from 52 to 62 the change is small, and we consider that CI-52 case is optimal.

#### B. Oscillator strengths of resonant transitions

We calculate oscillator strengths for well-studied experimentally and theoretically resonant argon transitions. The upper and lower panels of Fig. II show data for the [3p$^3/2$ 4s]$_1$ and [3p$^1/2$ 4s]$_1$ states, respectively. The agreement with SD CC calculations is excellent and most experiments is very close. For the weaker transition, deviation from the SD CC theory is somewhat larger, which is due to cancellation of contributions from different configurations. Such cancellation was more complete in neon, where we observed larger disagreement with the theory of Ref. 7.
C. Energies of argon even J=2 states

Table III shows our calculated energies for J=2 even states. For unique specification of levels, accurate NIST energies are provided. All energies are expressed in atomic units. ∆ is the deviation from experiment for the 7th level.

D. Argon transitions between excited states

Table IV shows the comparison of our calculations with experiments for line strengths between J=1 odd and J=2 even state transitions. Very large disagreement is observed when no RPA correction is added. However, if conventional RPA correction (Eq(1)) is included, the difference is also large, though of an opposite sign. And only if we include the appropriate, modified-denominator RPA correction (mRPA), which constitutes roughly a half of the conventional RPA correction, do our values agree with experiment at the level of the experimental accuracy. The experimental accuracy in Table IV is denoted by letters in accordance with the NIST convention: for example, the accuracy of class “C” is about 10%. Still in the case of the p^3_s1s transition the disagreement is quite large and independent of RPA corrections which might indicate that the problem is in the experiment. If we exclude this case and the inaccurate measurement of class “D”, then mRPA calculations can be considered accurate at the level of 10-20%.

We also compare our final results (mRPA calculations) with some available semiempirical calculations by Lilly.
which is defined as $\Delta = (S_{\text{exp.}} - S_{\text{theory}})/S_{\text{exp.}}$.

### TABLE IV: Line strengths in atomic units for transitions between J=1 odd and J=2 even states. Accuracy of experiments is shown as letters in accordance with the NIST convention [30]. Three cases with respect to RPA corrections are considered: “cRPA” (conventional), “nRPA” (no), and “mRPA” (modified-denominator) RPA corrections are included. The deviation from experiment is measured by $\Delta$, which is defined as $\Delta = (S_{\text{exp.}} - S_{\text{theory}})/S_{\text{exp.}}$.

| Transition | $\lambda$, Å | Exp. Ac. | cRPA | mRPA | mRPA | $\Delta$ |
|------------|-------------|----------|------|-------|-------|---------|
| $^3p_{3/2}$ 4s-p$_n$ 5p | 4301 | 0.074 C | 0.016 0.15 0.062 -16% |
| $^3p_{3/2}$ 4s-p$_n$ 5p | 4267 | 0.060 C | 0.025 0.079 0.048 20% |
| $^3p_{3/2}$ 4s-p$_n$ 5p | 4046 | 0.054 C | 0.025 0.099 0.054 0% |
| $^3p_{3/2}$ 4s-p$_n$ 5p | 4301 | 3.40 C | 3.41 4.26 3.79 -12% |
| $^3p_{3/2}$ 4s-p$_n$ 5p | 4267 | 0.060 C | 0.025 0.079 0.048 20% |
| $^3p_{3/2}$ 4s-p$_n$ 5p | 4046 | 0.054 C | 0.025 0.099 0.054 0% |

### TABLE V: Comparison of transition rates for transitions between excited states of argon. In Fig. 2 we compare our theoretical value with many available experimental values. While six experiments support NIST quoted value, a greater number of experiments support our theoretical value. Therefore, we tend to conclude that NIST values can be somewhat wrong. We also find that semiempirical calculations are not able to predict these particular experiments; namely, most extensive semiempirical calculations [1] give the transition rate $1.33 \times 10^6 \text{s}^{-1}$ that disagrees with all experiments. Returning to our Table IV we can argue that some large deviations of our theory from experiment can be caused by inaccuracy of quoted experimental errors.

For better tests of our theory, more accurate experi-

- Garstang and Blerkom [2]
- Wende [3]
- Bues et al. [4]
- Jones and Wiese [5]
ments are needed. For this reason, we have measured the ratio of line strengths using an accurate laser absorption technique [42]. Our experimental ratio, 3.29 ± 0.13, for the two transitions at 9787 Å and 9227 Å completely agrees with our theoretical value, 3.22. It would be extremely interesting if this experimental technique was further developed and applied to other transitions in argon or in other noble gas atoms. For example, experiments in neon using visible lasers could test the accuracy of this experimental method, since our theory is expected to be more accurate in neon than in argon.

IV. CONCLUSIONS

In this paper, we have applied CI+MBPT theory to calculate energies and transition properties of argon particle-hole states. Our theoretical energies and transition rates are in good agreement with most experiments. We found that random-phase approximation corrections are essential. We also analyzed dependence of accuracy on the size of configuration space and determined the optimal size of CI matrix. Our CI+MBPT program can be used for calculations of many other transitions of closed-shell atoms and ions.

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