Ab initio oscillator strengths for transitions between $J=1$ odd and $J=1,2$ even excited states of Ne I

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Ab initio theory is developed for radiative transitions between excited states of neon. Calculations of energies for even excited states $J=1$, $J=2$ supplement our previous calculations for $J=1$ odd excited states. Line strengths for transitions between $J=1$ odd and $J=1,2$ even states of Ne I are evaluated. A comparison with experiments and semiempirical calculations is given.

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I. INTRODUCTION

Development of *ab initio* theories for neutral open-shell atoms is a difficult task, since the interaction between electrons of an open shell is strong and cannot be treated perturbatively. Nevertheless, some progress in two and even three-valence electron atoms has been achieved with the combination of the configuration-interaction (CI) method and many-body perturbation theory (MBPT) [1–3]. Particle-hole states of closed-shell atoms have the additional difficulty that conventional perturbation theory does not converge for hole states. We solved the convergence problem by modifying denominators [3,4]. As a result, we were able to achieve agreement with experiment for neon energies of $J=1$ odd excited states and oscillator strengths (averaged over many measurements) of transitions to the ground state. In this paper, we extend our application of the CI+MBPT method to neon transitions between excited states. If we succeed, our understanding of the neon atom and low-Z neonlike ions will be substantially improved.

Fairly accurate (about 5%) measurements of many transition rates between excited states are available, providing important tests of theory. In addition, semiempirical calculations can be compared with our calculations. For example, many transition rates along the neon isoelectronic sequence were calculated by Hibbert *et al.* [5] with a general configuration-interaction code (CIV3) [6]. In calculations, a few parameters were adjusted to fit experimental energies. However, even after such adjustments, the results still disagreed significantly with other semiempirical calculations by Seaton [7] and with experiments. The latter theory was more successful, giving results in close agreement with experiments. No pure *ab initio* theory, as far as we know, was (successfully) applied previously to calculations of transitions between neon excited states. For transitions to the ground state, elaborate *ab initio* calculations exist (Avgoustoglou and Beck [8]), but agreement with experiment for an oscillator strength of the $[2p_{3/2}^{-1}3s_{1/2}]_1$ neon state is unsatisfactory. These calculations are more effective in heavier noble-gas atoms, where the agreement with experiment is achieved for Ar, Kr, and Xe atoms. In neon, on the other hand, our calculations with the CI+MBPT method give results close to the average experimental values.

It is a well-known fact that neon transitions between excited states are sensitive to the accuracy of fine-structure splittings. Semiempirical theories avoid this difficulty by introducing and adjusting several parameters to match energies of multiplets as precisely as possible. For example, using the quantum defect method, Seaton [7] was able to obtain very small root-mean-square deviations for energies. As a result, he also was able to obtain transition oscillator strengths that agree well with experiment. Getting accurate fine-structure intervals without parametric adjustments is a challenging task. We will demonstrate in this paper that CI calculations corrected with the second-order MBPT give energies and oscillator strengths for transitions between excited states with the precision comparable to the precision of the best semiempirical calculations.

The transition data in neon and other noble gases are needed for plasma physics and studies of discharges with many industrial applications in lamps and gas lasers. The opacity project [9] is another motivation behind many calculations (one example is given in Ref. [10]) in neonlike ions. Understanding of the neon atom can be beneficial for the development of atomic structure methods, which are needed for many applications. One important application of atomic structure is the calculations of parity-nonconservation amplitudes in heavy atoms with one or a few valence electrons, which require a clear understanding of correlation effects in these atoms. One-valence-electron MBPT has convergence problems similar to the hole MBPT after a core is excited. Modification of denominators according to our prescription might be one key to the solution of a puzzling problem that the third-order energy in Cs agrees worse with experiment than second-order energy. Calculations of the effects of the electron electric dipole moment in particle-hole atoms is another, more direct application of our particle-hole theory. Furthermore, the CI+MBPT method and convergent hole perturbation theory can be generalized for more complicated atoms with more than one particle or hole, and the properties of these atoms can be explored beyond the Hartree-Fock approximation.

In this paper, first we will briefly describe our method of calculations (more details are given in Refs. [3,4]); then, we will compare the CI+MBPT and experimental energies for $J=1$ and $J=2$ even states. This comparison gives an estimate on the accuracy of our wave functions. Next, we will

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show our results for transition line strengths. Finally, we compare our theory with other semiempirical calculations and experiments.

II. CI+MBPT CALCULATIONS

A. Energies and oscillator strengths for $J=1$ odd neon states

The Rayleigh-Schrödinger variant of second-order MBPT, given in Ref. [11], has low accuracy for neon (does not improve lowest-order approximation); therefore we developed a fast convergent variant of the MBPT [3,4]. This perturbation theory can be understood from couple-cluster single-double equations [12]. Simply put, we modify some denominators in the perturbation terms to take into account the strong interaction between a hole and a core electron or between core electrons nonperurbatively. The advantage of this approach compared to the couple-cluster method of Ref. [12] is the simplicity and speed of calculations. With our fast convergent MBPT method, we are able to improve the accuracy of hole energies and fine-structure splittings of light neonlike ions already after adding second-order MBPT corrections. 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 (the analysis of these small corrections is given in Ref. [12]).

To calculate particle-hole energies, we construct a model CI space [11], compute the effective Hamiltonian in this space, which also includes second-order MBPT corrections, and solve an eigenvalue problem. Along with energies we obtain wave functions, which were used to calculate oscillator strengths for transitions to the ground states [3,4]. The energies of neon particle-hole $J=1$ odd states and oscillator strengths were in very good agreement with experiment after using a relatively small CI space, 52. Pure *ab initio* 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 improved to the level of 0.0001 a.u. for almost all states. We will use the same wave functions for $J=1$ odd states in our calculations of transitions from $J=1$ odd to $J=1$ and $J=2$ even states. The accuracy of energies of even states involved in the transitions will be illustrated below.

B. Energies for $J=2$ and $J=1$ even neon states

In this section we present our calculations of energies for even states. We use the same formalism and numerical method as in Refs. [3,4]. The spline cavity is chosen to be 80 a.u., the number of splines is chosen to be 40, and the maximum orbital momentum is chosen to be 5. For excited states, a V^{N-1} Hartree-Fock (HF) potential basis (see Ref. [3]) is built from the HF V^N spline basis by the diagonalization of a one-electron Hamiltonian to take into account the major part of the interaction of an excited electron with a hole. Such a procedure speeds up the convergence of CI and reduces uncertainty in the denominators of a perturbation theory. A V^{N-1} HF basis used in Ref. [12] was constructed by solving differential HF equations and gives similar results, but our basis does not require rewriting the HF code and therefore is more convenient. The calculations of energies are shown in two tables.

TABLE I. Calculations of neon energy levels for $J=1$ even states. In the third and forth columns, ''CI-8'' and ''CI-32'' mean that in our calculations the size of the CI matrices were 8 and 32, respectively. Δ is the difference between theoretical and experimental energies. All energies are in atomic units.

$J=1$ even	NIST	CI-8	CI-32	Δ	Shifted Δ
$p_{3/2}^{-1}3p$	0.67551	0.6687	0.6690	0.0065	0.0005
$p_{3/2}^{-1}3p$	0.68400	0.6789	0.6787	0.0053	−0.0007
$p_{1/2}^{-1}3p$	0.68696	0.6820	0.6817	0.0052	−0.0008
$p_{1/2}^{-1}3p$	0.68818	0.6833	0.6830	0.0052	−0.0008
$p_{3/2}^{-1}4p$	0.74048	0.7337	0.7339	0.0066	0.0006
$p_{3/2}^{-1}4p$	0.74274	0.7370	0.7367	0.0060	0.0000
$p_{1/2}^{-1}4p$	0.74567	0.7398	0.7396	0.0061	0.0001
$p_{1/2}^{-1}4p$	0.74590	0.7402	0.7399	0.0060	0.0000

In Table I we compare with experiment our theoretical energies of $J=1$ even states. Energies calculated in a model space of size 32 agree better with experiment than energies calculated in a smaller size (8) model space. CI space 32 can be considered as optimal since a larger number of configurations does not improve much accuracy. Note that the size of the optimal CI space depends on the choice of a starting potential, since inadequate initial approximation is corrected by the diagonalization of the CI matrix. A 1% systematic shift is present, which can be attributed to the inaccuracy of hole energies; however, this shift does not affect much the accuracy of transition rates and is relatively unimportant. More important for weaker transitions is the fact that after subtracting this shift, we obtain very small residual deviations, which bode well for the accuracy of singlet-triplet mixing coefficients and transition amplitudes.

Similar agreement of energies is obtained for $J=2$ even states in Table II. Again, we have almost the same systematic shift, and after its subtraction, only a very small difference between experimental and theoretical energies remains. Therefore, we have reason to expect good precision for transitions between the excited states, which are considered next.

C. Transitions between neon excited states

Previously, we calculated oscillator strengths for the transitions to the ground state; the formula for excited-state tran-

TABLE II. Calculations of neon energy levels for $J=2$ even states. The size of the CI matrix is 32. Δ is the difference between theoretical and experimental energies. All energies are in atomic units.

$J=2$ even	NIST	CI-32	Δ	Shifted Δ
$p_{3/2}^{-1}3p$	0.68265	0.6775	0.0051	−0.0007
$p_{3/2}^{-1}3p$	0.68489	0.6800	0.00487	−0.0009
$p_{1/2}^{-1}3p$	0.68736	0.6825	0.00485	−0.0010
$p_{3/2}^{-1}4p$	0.74222	0.7363	0.00588	0.0001
$p_{3/2}^{-1}4p$	0.74285	0.7372	0.00565	−0.0001
$p_{1/2}^{-1}4p$	0.74591	0.7401	0.00578	−0.0000

TABLE III. Transitions between neon excited states, from $J=1$ odd to J=1 even. $p_{3/2}^{-1}$ and $p_{1/2}^{-1}$ are hole states, and particle states are immediately to the right. For unique specification, experimental wavelengths are also provided. The sizes of model space for even states are given, but for $J=1$ odd states the size is 50, the same in all cases. The experimental NIST and theoretical line strengths (in columns ''CI-8'' and ''CI-32'') are expressed in a.u.; Δ denotes the relative deviations of the theoretical line strengths from the experimental line strengths.

Transitions	λ(Å)	NIST	Acc.	CI-8	CI-32	+RPA	Δ (%)
$p_{3/2}^{-1}3s$-$p_{3/2}^{-1}3p$	6385	12.4	*B*-	12.5	12.6	12.2	2
$p_{3/2}^{-1}3s$-$p_{1/2}^{-1}3p$	6032	1.82	*B*-	1.83	1.88	1.81	1
$p_{3/2}^{-1}3s$-$p_{1/2}^{-1}3p$	6130	0.23	*B*-	0.32	0.23	0.22	4
$p_{3/2}^{-1}3s$-$p_{3/2}^{-1}4p$	3502	0.076	*D*	0.114	0.102	0.084	11
$p_{3/2}^{-1}3s$-$p_{3/2}^{-1}3p$	7247	5.27	*B*-	5.99	5.93	5.70	8
$p_{1/2}^{-1}3s$-$p_{3/2}^{-1}3p$	8085	0.094	*B*	0.121	0.107	0.103	10
$p_{1/2}^{-1}3s$-$p_{3/2}^{-1}4p$	3687	0.029	*D*	0.038	0.040	0.032	10
$p_{1/2}^{-1}3s$-$p_{1/2}^{-1}3p$	6601	9.88	*B*-	9.16	9.25	8.92	10
$p_{1/2}^{-1}3s$-$p_{3/2}^{-1}3p$	7026	0.971	*B*	0.825	1.01	0.982	1
$p_{1/2}^{-1}3s$-$p_{1/2}^{-1}3p$	6719	9.75	*B*-	11.0	10.9	10.5	8
$p_{1/2}^{-1}3s$-$p_{1/2}^{-1}4p$	3595	0.045	*D*	0.070	0.065	0.053	18
$p_{1/2}^{-1}3s$-$p_{1/2}^{-1}4p$	3601	0.030	*D*	0.050	0.045	0.036	21

sitions is different. The final expression for the coupled reduced matrix element after angular reduction in the *j*-*j* relativistic basis has the following form:

$$\langle F\|Z_J\|I\rangle = \sqrt{[J_F][J_I]}C_F(a'v')C_I(a,v) \times\left[(-1)^{J+J_I+j_a+j_{v'}}\begin{Bmatrix} J_I & J & J_F \\ j_{v'} & j_a & j_v \end{Bmatrix} \times\delta_{a'a}\langle v'\|Z_J\|v\rangle + (-1)^{J_F+j_{a'}+j_{v'}+1} \times\begin{Bmatrix} J & J_I & J_F \\ j_v & j_{a'} & j_a \end{Bmatrix}\delta_{v'v}\langle a\|Z_J\|a'\rangle\right].$$

We use standard notations of relativistic MBPT methods, see, for example Ref. [14]. Configuration weights of the final $C_F(a'v')$ and the initial $C_I(a,v)$ states are obtained in CI calculations. Note that this formula is different from that for the transitions between two-particle states [14] even if we neglect small hole-hole matrix elements. However, it is possible to modify wave functions to use two-particle matrix elements, which can be convenient if the program for calculations of two-particle matrix elements is available.

TABLE IV. Line strengths (a.u.) for transitions between neon excited states from $J=1$ odd to $J=2$ even. Abbreviations are the same as in Table III .

Transitions	λ Å	NIST	Acc.	CI-32	+RPA	Δ (%)
$p_{3/2}^{-1}3s$-$p_{1/2}^{-1}3p$	6097.8507	10.1	C+	10.2	9.76	3
$p_{3/2}^{-1}3s$-$p_{3/2}^{-1}3p$	6508.3259	20.4	B-	21.1	20.2	1
$p_{3/2}^{-1}3s$-$p_{3/2}^{-1}3p$	6306.5325	2.57	B-	2.54	2.62	2
$p_{3/2}^{-1}3s$-$p_{3/2}^{-1}4p$	3516.1960	0.074	D	0.106	0.077	4
$p_{1/2}^{-1}3s$-$p_{3/2}^{-1}4p$	3702.2783	0.028	D	0.034	0.029	4
$p_{1/2}^{-1}3s$-$p_{1/2}^{-1}3p$	6680.1202	17.1	C+	16.9	17.1	0
$p_{1/2}^{-1}3s$-$p_{3/2}^{-1}3p$	6931.3788	14.3	B-	16.6	15.3	7
$p_{1/2}^{-1}3s$-$p_{1/2}^{-1}4p$	3594.5516	0.11	D	0.14	0.11	0
$p_{1/2}^{-1}3s$-$p_{3/2}^{-1}3p$	7175.9155	2.62	B-	2.51	2.61	0

Tables III and IV show our results of calculations for $J=1\rightarrow J=1$ and $J=1\rightarrow J=2$ excited-state transitions. Many precisely measured (5% level) neon transition rates provide an important test of accuracy of our calculations. In Table III, the calculations are done with two configurations to show an improvement in precision for the larger number of configurations. Important random-phase approximation (RPA) corrections are included by replacing the ''bare'' matrix elements with ''dressed'' RPA matrix elements (the replacement for two-valence electron atoms was implemented in Refs. [2,3]). Including RPA corrections needs some care, because a hole state present when the transition between excited states occurs leads to the convergence problem and low accuracy of the regular RPA corrections. Our standard cure is to modify denominators by subtracting the radial Slatter integral $R_0(abab)$, thus taking into account the monopole interaction of a hole with a core electron. This modification of denominators approximately halves RPA corrections. Adding divided by 2 normal RPA corrections, we estimated the level of these corrections and found that they are important, and improve agreement with experiment. In neon, the corrections constitute a few percent of a total matrix element, but in heavier noble-gas atoms, they are even larger and more important. In the last column, we place our best values calculated in CI-32 model space with appropriate modified-denominator RPA corrections.

The deviation from experiment is consistent with the experimental accuracy (for example, the accuracy of class *B* is in the range 5% and the deviation from theory is of the same magnitude). For transitions that have the experimental accuracy of classes *B*− and *C*+, the theory is as accurate as or even more accurate than the experiment, but for class *D*, the theory is definitely more accurate. Still the accuracy of the theory is not the same for all transitions, since some suppressed transitions owing to cancellation could be more sensitive to fine-structure splittings.

Our final table (Table V) contains our best values of oscillator strengths with the RPA corrections for comparison with experiments and other theories. Oscillator strengths are calculated from line strengths *S* and transition energies ω in atomic units,

$$f=\tfrac{2}{3}\omega S. \tag{1}$$

Due to a large number of measurements and calculations, we restricted ourselves to comparison with results from a few sources, which contain further references; for example, references to many experiments and comparison with several measurements are given by Bridges and Wiese [13], where the authors also estimated the uncertainties of their experi-

TABLE V. Comparison of experimental and theoretical oscillator strengths of neon. We adopt compact notations of Ref. [7]: $p_i q_i r_i - p_f q_f r_f$, where $p=2j_a$, $q=2K$, $r=J$, i stands for initial, and f stands for final. The hole angular momentum j_a is coupled with the orbital momentum of the excited electron l to give the angular momentum K in the intermediate coupling scheme; K is coupled with the spin of the excited electron to give a total angular momentum of particle-hole state J. For complete specification, nl quantum numbers are also provided. Brackets denote powers of 10.

Transitions	λ Å	NIST	Ref. [13]	Present paper	Ref. [7]	Ref. [5]
3*s*-3*p* 331−132	6097	5.03[−1]	4.98[−1]	4.86[−1]	4.88[−1]	5.49[−1]
3*s*-3*p* 331−352	6508	9.52[−1]	9.46[−1]	9.43[−1]	9.27[−1]	1.03[0]
3*s*-3*p* 331−332	6307	1.24[−1]	1.26[−1]	1.26[−1]	1.26[−1]	1.20[−1]
3*s*-4*p* 331−352	3516	6.39[−3]		6.65[−3]	6.22[−3]	
3*s*-4*p* 111−352	3702	2.30[−3]		2.38[−3]	2.27[−3]	
3*s*-3*p* 111−132	6680	7.78[−1]	7.71[−1]	7.78[−1]	7.78[−1]	8.18[−1]
3*s*-3*p* 111−332	6931	6.27[−1]	6.27[−1]	6.71[−1]	6.34[−1]	6.16[−1]
3*s*-4*p* 111−132	3595	9.29[−3]		9.29[−3]	8.59[−3]	
3*s*-3*p* 111−352	7176	1.11[−1]	1.24[−1]	1.10[−1]	1.18[−1]	1.30[−1]
3*s*-3*p* 331−331	6385	5.90[−1]	5.81[−1]	5.78[−1]	5.81[−1]	6.45[−1]
3*s*-3*p* 331−111	6032	9.17[−2]	8.36[−2]	9.11[−2]	8.57[−1]	7.79[−2]
3*s*-3*p* 331−131	6130	1.14[−2]	1.19[−2]	1.09[−2]	1.12[−2]	2.49[−2]
3*s*-4*p* 331−331	3502	6.59[−3]		7.29[−3]	6.60[−3]	
3*s*-3*p* 331−311	7247	2.21[−1]	2.36[−1]	2.39[−1]	2.21[−1]	2.46[−1]
3*s*-3*p* 111−311	8085	3.53[−3]	3.53[−3]	3.87[−3]	3.02[−3]	3.60[−3]
3*s*-4*p* 111−331	3687	2.39[−3]		2.64[−3]	2.42[−3]	
3*s*-3*p* 111−111	6601	4.55[−1]	4.41[−1]	4.10[−1]	4.42[−1]	
3*s*-3*p* 111−331	7026	4.20[−2]	4.35[−2]	4.25[−2]	4.43[−2]	3.69[−2]
3*s*-3*p* 111−131	6719	4.41[−1]	4.41[−1]	4.76[−1]	4.42[−1]	3.70[−1]
3*s*-4*p* 111−111	3595	3.80[−3]		4.48[−3]	4.32[−3]	
3*s*-4*p* 111−131	3601	2.53[−3]		3.07[−3]	2.55[−3]	

ment to be about 7% and of the others shown in their comparison table to be in the range 10–50%. The experiments seem to be in good agreement. NIST data derived from various sources are in close agreement with values given by Bridges and Wiese [13]. The agreement with experiment of the semiempirical theory by Seaton [7] is similar to the agreement of our *ab initio* theory. Calculations performed by Hibbert *et al.* [5] agree worse; for example, for the 6130-Å transition, an experimental value is 0.0114 or 0.0119, our value is 0.0109, but the value in Ref. [5] is 0.0249. Overall agreement of theories and experiments is quite normal.

III. CONCLUSIONS

In this paper, we have applied the CI+MBPT for particle-hole states of closed-shell atoms to calculations of transitions between excited states of neon. A difficulty that the hole energy has poor convergence is overcome with modifications of denominators in the MBPT. Good precision for particle-hole states is illustrated for many energy levels of neon. Apart from energies, our theory is tested in calculations of line strengths. Agreement with experimental values is achieved.

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