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ScienceDirect
International Journal of Mass Spectrometry 271 (2008) 85–92
International Journal of Mass Spectrometry
www.elsevier.com/locate/ijms

Multiconfiguration Dirac–Hartree–Fock energies and transition probabilities for $2p^4(^3P)3d$–$2p^4(^3P)4f$ transitions in Ne II

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Received 13 August 2007; received in revised form 8 September 2007; accepted 10 September 2007
Available online 14 September 2007

Abstract

Multiconfiguration Dirac–Hartree–Fock energies, lifetimes, and transition probabilities for transitions between $2p^4(^3P)3d$ and $2p^4(^3P)4f$ levels of Ne II are reported from calculations that included the effect of core-polarization. Transition energies are in excellent agreement with observed values. For many transitions the length and velocity gauge results agree within a fraction of a percent. Transition probabilities are compared with experimental values and the Coulomb approximation.

PACS: 31.15.Ar; 31.15.Ne; 31.30.Jv; 32.70.Cs

Keywords: Atomic structure; Multiconfiguration Dirac–Hartree–Fock method; Energy levels; Transition probabilities; Ne II

1. Introduction

In an article on the expanding Atomic Spectra Database (ASD) at the National Institute of Standards and Technology (NIST), Wiese [1] cites the 3p–3d transition array in Ne II as an example of an unsettled case. In spite of sophisticated calculations and a number of experimental measurements, large unresolved differences remained. Recently new measurements of branching fractions from some levels for which lifetime data were available have been reported [2]. The determination of all downward transitions in that experiment included a number of weak intersystem lines as a valuable check on theory. Closer agreement with multiconfiguration Hartree– Fock + Breit–Pauli (MCHF + BP) results [3] was found than had been the case with earlier experiments.

An equally unsettled case is the 3d–4f transition array. Because the exchange Slater integrals for $2p^4 4f$ are even smaller than for $2p^4 3d$, the LS terms are also more closely spaced and extensive term mixing occurs. Whereas the energy levels of $2p^4(^3P)3d$ span an energy range of $2582\,cm^{-1}$ [4], those of $2p^4(^3P)4f$ span a range of only $996\,cm^{-1}$, and ASD levels are designated in [jK] notation in the absence of meaningful LSJ designations. In the present paper, energy levels, lifetimes, and transition probabilities for $2p^4(^3P)3d$–$2p^4(^3P)4f$ are reported using the multiconfiguration Dirac–Hartree–Fock (MCDHF) method, in which relativistic effects are included directly. At the same time, since both 3d and 4f are outer electrons well separated from the $2p^4$ core, a core-polarization computational model was selected. The calculated wavelengths are compared with the most recent compilation of atomic data for Ne II [5].

2. The computational procedure

The theoretical basis of our computation was the MCDHF method [6] as implemented in the GRASP2K computer code [7] and using the core-polarization model. This model has proven to be very effective for computing $2p^4(^3P)3p$–$2p^4(^3P)3d$ transitions in Ne II. In Ref. [8] theoretical results are compared for two types of calculations: MCDHF for which transition rates are reported in both length and velocity gauges, and MCHF + BP with transition rates only in the length gauge. In spite of the fact that MCHF + BP energies are in better agreement with observations, the experimental transition probabilities obtained by del

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doi:10.1016/j.ijms.2007.09.003

Val et al. [9] for 3p–3d transitions was found to be in better agreement with MCDHF values.

The core-polarization model is expected to be appropriate also for 3d–4f transitions. The $2p^4(^3P)3d$ and $2p^4(^3P)4f$ levels have a common parent. Although there is a spin–orbit interaction between $2p^4\ ^3P_2$ and $2p^4\ ^1D_2$, the interaction is not strong. The similar interaction between $2p^4\ ^3P_0$ and $2p^4\ ^1S_0$ is even weaker. A parent changing transition would need to account correctly for the separation between the different parent energies. For the present parent preserving transitions, it is expected that MCDHF will adequately account for the spin–orbit interactions between the different parents, even though the energy separation may not be accurate.

In the MCDHF procedure, the wave function Ψ for the atomic state labeled γJ is approximated by an expansion over *jj*-coupled configuration state functions (CSFs):

$$\Psi(\gamma J) = \sum_j c_j \Phi(\gamma_j J), \tag{1}$$

where the CSFs $\Phi(\gamma J)$ are anti-symmetrized linear combinations of relativistic orbital products of the form:

$$\phi(\mathbf{r}) = \frac{1}{r}\begin{pmatrix} P_{n\kappa}(r)\chi_{\kappa m}(\hat{r}) \\ iQ_{n\kappa}(r)\chi_{-\kappa m}(\hat{r}) \end{pmatrix}. \tag{2}$$

Here κ is the relativistic angular momentum, $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$ are the large and small component radial wave functions and $\chi_{\kappa m}(\hat{r})$ is the spinor spherical harmonic. After obtaining the set of radial functions, relativistic configuration interaction (CI) calculations are carried out to determine CSF expansion coefficients by diagonalizing the Hamiltonian matrix that includes the frequency dependent Breit interaction and vacuum polarization correction. Transition probabilities between levels with separately optimized wavefunctions are computed using biorthogonal transformations [10].

In the core-polarization model, the wave function is an expansion over the set of either odd or even configuration states $2s^22p^4nln'l'$ and $2s2p^5nln'l'$, where nl and $n'l'$ are orbitals from an orbital set. In our work, the 1s,2s,2p orbitals for the parent states were determined from extended optimal level (EOL) calculations for the $^3P_{0,1,2}$ and $^1D_2$ terms of $2p^4$. These orbitals were then kept fixed for both the odd and even states. The remaining orbitals were obtained through a process that took into account the spectrum while building an orbital basis. We will refer to the {1s,2s,2p, ..., 3s,3p,3d} set of orbitals as the $n = 3$ orbital set, {1s,2s,2p, ..., 4s,4p,4d,4f} as $n = 4$, etc. However, for $n > 5$ the highest angular momentum for an orbital was $l = 4$, or a *g*-orbital. Calculations were done successively for $n = 3, \ldots, 7$, and each time only the new "layer" of orbitals was optimized for a selected set of atomic states.

For the even states, the $n = 3$ orbitals were optimized on all the states of $2p^43s$ and $2p^4(^3P)3d$, where all parents are included unless indicated otherwise. Thus, at the $n = 3$ level of the calculation, only 3p is a correlation orbital in the core-polarization expansion. The $2s2p^6\ ^2S_{1/2}$ state was omitted from the optimization. At $n = 4$, the $2p^4(^3P)4s$ and $2p^4(^3P)4d$ states were added to the optimization set with only 4p and 4f as correlation orbitals. At $n = 5$, $2p^4(^3P)5s$ and $2p^4(^1D)3d$ states were added to the optimization set, with 5p, 5d, 5f, 5g all being correlation orbitals. For $n = 6$ and 7 all orbitals were correlation orbitals, and the optimization set remained unchanged.

For the $n = 3$ odd state calculation, the orbitals were optimized on all the states of $2p^43p$ and omitting the $2p^5\ ^2P^o$ ground state. The 3p orbital was required to be a spectroscopic orbital with the usual nodal structure. The $n = 4$ calculation added the $2p^4(^3P)4p$ and $2p^4(^3P)4f$ states with 4p and 4f required to be spectroscopic. No new states were added to the optimization set of states for $n = 5, 6, 7$ and all orbitals were correlation orbitals of arbitrary nodal structure.

In these optimization calculations, the Dirac–Coulomb Hamiltonian was used in the variational self-consistent field procedure. Once the radial basis had been obtained, a relativistic configuration interaction (CI) calculation was performed that included the frequency dependent Breit correction, the vacuum polarization, and the QED correction. The wave functions were then used to obtain all the E1 transitions between the computed states, from which lifetimes could be determined. The *ab initio* results of all these calculations are available at http://atoms.vuse.vanderbilt.edu[11].

3. Results and evaluation of data

In this paper, we are concerned primarily with the $2p^4(^3P)3d$–$2p^4(^3P)4f$ transitions. No other theoretical data is available except for some Coulomb approximation results published in a 1966 NIST compilation [12] where LS coupling was used for determining the multiplet components. Table 1 reports the energy levels, splitting of the multiplet relative to the lowest level, difference between theoretical and observed energy levels, and lifetimes of the $2p^4(^3P)3d$ and $2p^4(^3P)4f$ levels.

Because the core-polarization model includes $2p^2 \rightarrow nln'l'$ excitations in the ground state but not in the excited states, the correlation in the present calculation is unbalanced and the energy of the ground state is too low. Consequently, the energy levels of the spectrum shown in Table 1 were adjusted so that the lowest $2p^4(^3P)3s\ ^4P_{5/2}$ agreed with the observed level. This shift, which does not affect 3d–4f transition energies, was not included at the website [11] where transitions from the ground state also are included.

The *jj*-coupling used by GRASP, identifies a state by J, parity, and an index for the eigenvalue of the computed interaction matrix. The wave function composition is distributed over many *jj*-coupled configuration states and it is customary to assign state labels by J and parity in the same order as ASD. In Breit–Pauli calculations the dominant configuration, LS term, and J are usually readily identified. This is the case for $2p^4(^3P)3d$ when accurate wave functions have been determined. A number of studies [8,13,3] have shown that the $^2F_{7/2}$ level is lower in the spectrum than $^4F_{7/2}$, whereas the earlier ASD classification, based on simpler procedures, had the levels reversed. The latest compilation [5] is now in agreement with theory. By comparison of g_J values from MCHF + BP calculations that include correlation in the $2s^22p^4$ core as well as core-polarization [3]