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Near Degeneracy Effects on the Low-Lying Spectrum of the Iron Atom

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The ground state and the LS terms coming from the ground-state configuration, $[Ar]-3d^6 4s^2$, of the iron atom are studied by carrying out an all electron Variational Monte Carlo calculation. Explicitly correlated trial functions including near degeneracy effects are used. The effect of electronic correlations and the importance of near degeneracy effects are systematically analyzed for the states here considered and compared with the experimental values. Correlations are important to reproduce, even qualitatively, the low-lying spectrum of this atom. A significant quantitative improvement when comparing with the experimental values is achieved when near degeneracy is considered along with dynamic correlations in the variational trial wave function. Finally, the effect of relativity on the results here reported is discussed.

Introduction

The $[Ar]-3d^6 4s^2$ and $[Ar]-3d^7 4s$ configurations play a very important role in the low-energy spectrum of the iron atom.[1] The ^5D ground state arises from the $3d^6 4s^2$ configuration, whereas the first excited states, ^5F, ^3F, and ^5P arise from the $3d^7 4s$ configuration. (The core [Ar] will be omitted in the notation from now on.) The subsequent levels coming from these configurations present a mixed order, with terms arising from either of the two configurations.

From a theoretical point of view, noncorrelated calculations give rise to excitation energies of the first excited states that are overestimated as compared with experimental values.[2,3] Electronic correlations play a very important role for the states arising from these configuration and, in general, for atoms with incomplete 3d and 4s subshells; see, for example, refs 4−7 and references therein. Therefore, large basis sets and very high levels of electron correlation are necessary to reproduce the relative ordering of the states.[8]

Explicitly correlated wave functions have shown to be a very convenient ansatz for describing electronic correlations in atomic systems.[9] These wave functions consist of a correlation Jastrow factor, F, multiplied by a model function, Φ. A number of free parameters to be optimized in a variational Monte Carlo (VMC) calculation are included in the trial wave function. Usually, a Jastrow factor including electron−electron and electron−nucleus distances is employed.[10] This function is completely symmetric with respect to the electron coordinates. The model function is usually taken as a linear combination of Slater determinants and accounts for both the antisymmetry of the total wave function and the angular momentum of the state. Single configuration model wave functions along with an energy optimized Jastrow factor have been shown to provide accurate VMC energies for atoms and single ionized cations[11−13] with $3 \leq Z \leq 54$.

In a previous work,[3] a VMC study of the ground state, $3d^6 4s^2 - {}^5D$, and of the low-lying excited states arising from the

configurations $3d^6 4s^2$ and $3d^7 4s$ was carried out by using a single configuration explicitly correlated trial wave function. Whereas, in general, a good description of the states under study was achieved, a different performance for the states arising from the two electronic configurations was observed. More correlation energy was recovered for the terms coming from the $3d^7 4s$ configuration than for the terms from the $3d^6 4s^2$ configuration. As a consequence, the excitation energy of the terms from the $3d^7 4s$ configuration is underestimated by 0.03 to 0.04 hartree (i.e., between 0.8 and 1 eV) for all of the states there studied. This leads to the fact that, for example, the lowest energy term coming from the $3d^7 4s$ configuration presents a VMC energy that coincides, within the statistical error, with that obtained for the ground state, whereas the experimental excitation energy is 0.032 hartree.[1]

To obtain a more realistic description of the levels of this atom, not only quantitatively but also qualitatively, nondynamic correlations need to be included within this scheme. There are atomic states for which two or more electronic configurations present a significant weight. This kind of correlations is harder to account for by means of a Jastrow factor. States displaying this feature require a multiconfiguration description to achieve the same degree of accuracy as that obtained for others with a stronger monoconfigurational character; see, for example, ref 12 and references therein. This is the case of the near degeneracy effect that appears in the states from the $3d^6 4s^2$ configuration. A more reliable description of these states can be obtained if the $3d^6 4p^2$ configuration is included in the trial wave function.

In this article, we study the near degeneracy effects in the low-energy spectrum of the iron atom by using the VMC method. The states studied are the ground state as well as the lowest energy LS terms coming from the $3d^6 4s^2$ configuration: $1\,^5D$, $1\,^3P$, $1\,^3H$, $1\,^3F$, $1\,^3G$, $1\,^1I$, $1\,^3D$, $1\,^1G$, $1\,^1D$, $1\,^1S$, and $1\,^1F$. As we shall see, the ground-state energy is lowered in such a way that the description of the excitation energy of the states from the $3d^7 4s$ configuration is improved. Atomic units are used throughout this work.

Wave Function

The correlated trial wave function, Ψ, used in this work is the product of a symmetric correlation factor, F, which includes

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TABLE 1: Total Energy in Atomic Units for the Different Terms of the Ground-State Configuration $3d^6 4s^2$ Calculated from a Trial Wave Function Including near Degeneracy Effects with a Jastrow Factor, $E_{J-MC(2)}$, and without Correlation Factor, $E_{MC(2)}$[a]

term	SC		MC2		J-SC		J-MC2		exptl
	E	E_{exc}	E	E_{exc}	E	E_{exc}	E	E_{exc}	
1 ^{5}D	−1262.43632	0.0	−1262.46676	0.0	−1263.3757(19)	0.0	−1263.4031(18)	0.0	0.0
1 ^{5}F	−1262.37090	0.65		0.96	−1263.3771(17)	−0.001(3)		0.026(3)	0.032
1 ^{3}F	−1262.34375	0.092		0.123	−1263.3590(28)	0.017(3)		0.044(3)	0.055
1 ^{5}P	−1262.29964	0.137		0.167	−1263.3205(37)	0.055(4)		0.082(4)	0.080
1 ^{3}P	−1262.32659	0.110	−1262.35624	0.110	−1263.2682(45)	0.107(5)	−1263.3040(35)	0.099(4)	0.084
1 ^{3}H	−1262.33781	0.098	−1262.36726	0.099	−1263.2826(43)	0.093(5)	−1263.3187(26)	0.084(3)	0.089
1 ^{3}F	−1262.32314	0.113	−1262.35280	0.114	−1263.2673(35)	0.108(4)	−1263.3151(33)	0.088(4)	0.094
1 ^{3}G	−1262.29345	0.143		0.173	−1263.3157(38)	0.060(4)		0.087(4)	0.099
1 ^{3}P	−1262.27221	0.164		0.194	−1263.3149(32)	0.061(4)		0.088(4)	0.104
1 ^{3}G	−1262.31137	0.125	−1262.34116	0.126	−1263.2512(35)	0.124(4)	−1263.2926(33)	0.110(4)	0.108
2 ^{3}P	−1262.26936	0.168		0.198	−1263.2924(32)	0.080(4)		0.107(4)	0.111
1 ^{1}G	−1262.27927	0.157		0.187	−1263.2982(46)	0.077(4)		0.105(5)	0.112
1 ^{3}H	−1262.26960	0.167		0.197	−1263.2931(33)	0.083(4)		0.110(4)	0.119
1 ^{3}D	−1262.26143	0.175		0.205	−1263.2787(37)	0.097(4)		0.124(4)	0.119
1 ^{1}P	−1262.25538	0.181		0.211	−1263.2793(34)	0.096(4)		0.123(4)	0.125
1 ^{1}D	−1262.24719	0.189		0.219	−1263.2785(31)	0.097(4)		0.124(4)	0.130
1 ^{1}H	−1262.25538	0.181		0.211	−1263.2838(33)	0.092(4)		0.119(4)	0.131
1 ^{1}I	−1262.28859	0.148	−1262.31823	0.148	−1263.2373(32)	0.138(4)	−1263.2672(38)	0.136(4)	0.134
1 ^{3}D	−1262.27470	0.162	−1262.30409	0.163	−1263.2304(31)	0.145(4)	−1263.2588(38)	0.144(4)	0.135
1 ^{1}G	−1262.28072	0.156	−1262.31026	0.156	−1263.2303(38)	0.136(4)	−1263.2673(31)	0.136(4)	0.136
1 ^{1}D	−1262.24122	0.195	−1262.27071	0.196	−1263.1979(48)	0.178(5)	−1263.2412(40)	0.162(4)	0.158
2 ^{3}F	−1262.19790	0.240		0.270	−1263.2216(28)	0.154(4)		0.181(3)	0.168
1 ^{1}S	−1262.25473	0.182	−1262.28432	0.182	−1263.2032(42)	0.173(4)	−1263.2411(34)	0.162(4)	
1 ^{1}F	−1262.20973	0.227	−1262.23953	0.227	−1263.1607(42)	0.215(4)	−1263.2087(38)	0.194(4)	

[a] Single configuration energies, E_{J-SC} and E_{SC}, for those states and for the terms arising from the $3d^7 4s$ taken from ref 3 are also shown. In parentheses, we show the error in the last Figure.

the dynamic correlation among the electrons, times a model wave function, Φ, that provides the correct properties of the exact wave function such as the spin and the angular momentum of the atom and is antisymmetric in the electronic coordinates

$$\Psi = F\Phi \qquad (1)$$

For the correlation factor, we use the form of Boys and Handy[14] with the prescription proposed by Schmidt and Moskowitz.[10]

$$F = \exp \sum_{i<j} U_{ij} \qquad (2)$$

where

$$U_{ij} = \sum_{k=1}^{N_c} c_k (\bar{r}_i^{m_k} \bar{r}_j^{n_k} + \bar{r}_i^{n_k} \bar{r}_j^{m_k}) \bar{r}_{ij}^{o_k} \qquad (3)$$

and

$$\bar{r}_i = \frac{br_i}{1 + br_i}, \quad \bar{r}_{ij} = \frac{dr_{ij}}{1 + dr_{ij}}$$

The coefficients b and d represent the inverse of the effective range of the correlation that has been fixed at the value of one atomic unit in the present calculation and c_k represents the variational parameters. We have worked with $N_c = 17$, including electron−nucleus, electron−electron, and electron−electron−nucleus correlations. The first coefficient is fixed to satisfy the

electron−electron cusp exactly, whereas the others are taken as variational parameters.

The model wave function has been fixed within the parametrized optimized effective potential (POEP) method extended for multiconfigurational wave functions.[15] The model wave function is written as

$$\Phi = \sum_k C_k \phi_k \qquad (4)$$

where ϕ_k is each one of the terms with the proper values of the total spin and orbital angular momentum arising from the configurations selected to describe a given state. A single configuration, SC, approach is used for the terms arising from the configuration $3d^7 4s$. For the states coming from the ground-state configuration, a two-configuration, MC(2), model wave function is employed. Both the $3d^6 4s^2$ and the $3d^6 4p^2$ configurations are included to take into account near degeneracy effects.

Once the model wave function is fixed, the Jastrow factor, F, is introduced, and the total energy of the term is minimized with respect to the c_k coefficients in eq 3 for both the single configuration, J-SC, and the two configuration, J-MC(2), trial wave functions obtaining different correlation factors for each model function. The c_k coefficients are calculated by using the algorithm of ref 16, which is based on the Newton method with analytical derivatives to calculate the gradient and the Hessian matrix. In the present work, the mixing coefficients of the configuration expansion are fixed at the POEP level, that is, without the Jastrow, because no significant gain in the energy was reached when optimizing these parameters along with those in the Jastrow factor. The correlation factors are optimized independently for each term.

The model wave function including these two configurations involves a large number of determinants and makes the Monte

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Carlo optimization very time-consuming. The calculations have been performed with a sampling size of 4×10^7 movements per particle for all excited states and of 1.2×10^8 movements per particle for the ground state. With this, the statistical error for the different states is similar to that obtained with a single configuration model wave function and a sampling size of 2×10^8 moves per particle for both the ^5D ground state and the ^5F first excited state and 4×10^7 movements per particle for all other excited states.[3]

Results

In Table 1, we report the results obtained for the different states from the $3d^64s^2$ configuration by using the two-configuration model function with and without the Jastrow correlation factor, J-MC(2), and MC(2) columns, respectively. The corresponding single configuration results,[3] J-SC and SC, and the results for the states arising from the $3d^74s$ configuration are also shown for the sake of comparison. The total energy, E, obtained by using the different wave functions as well as the excitation energy, E_{exc}, calculated from these results as compared with the experimental values[1] are shown.

The uncorrelated excitation energies, SC column, are overestimated with respect to the experimental values. In addition, the qualitative form of the spectrum is not reproduced. This is illustrated in Figure 1, where we plot some of the states of the low-lying spectrum of the iron atom arising from the $3d^64s^2$ and $3d^74s$ configurations. The values calculated from the different ansatz here analyzed are compared with the experimental values. Near degeneracy effects, column MC(2) in Table 1, lead to a roughly constant lowering on the energy for all of the states of ∼0.03 hartree. As the ground state arises from the $3d^64s^2$ configuration, the excitation energy of the states from the same configuration is practically unchanged in MC(2) with respect to the single configuration calculation. However, the excitation energy of the states from the $3d^74s$ configuration is increased by this quantity, and thus the agreement between theory and experiment gets worse after inclusion of near degeneracy effects. (See Figure 1.)

When the Jastrow factor is included in the single configuration scheme, J-SC, the excitation energy is, in general, reduced. This reduction improves the excitation energy of the states from the $3d^64s^2$ configuration, but it is not enough to reach the experimental values, and the excitation energy is still overestimated. The effect of dynamic correlations is more pronounced on the states from the $3d^74s$ configuration in such a way that the excitation energy of these states is reduced. Contrary to the case of the terms from the $3d^64s^2$ configuration, the excitation energy of the states from the $3d^74s$ configuration is underestimated in the J-SC approximation. For example, in this scheme, the ground-state energy and the energy of the lowest energy term from the $3d^74s$ configuration coincide within the statistical error.

When both, near degeneracy effects and dynamic correlations are included in the wave function, J-MC(2), the results are improved as compared with the experimental values. The ground-state energy is improved, and, as a consequence, the excitation energy of the states from the $3d^74s$ is enhanced, giving rise to a better comparison with experimental excitation energies. The effect on the terms from the $3d^64s^2$ configuration is to reduce the excitation energy, as compared with the J-SC, in such a way that again the results are improved, as can be seen in Figure 1. Therefore, both dynamic correlations and near degeneracy effect play an important role on the low-lying spectrum of this atom.
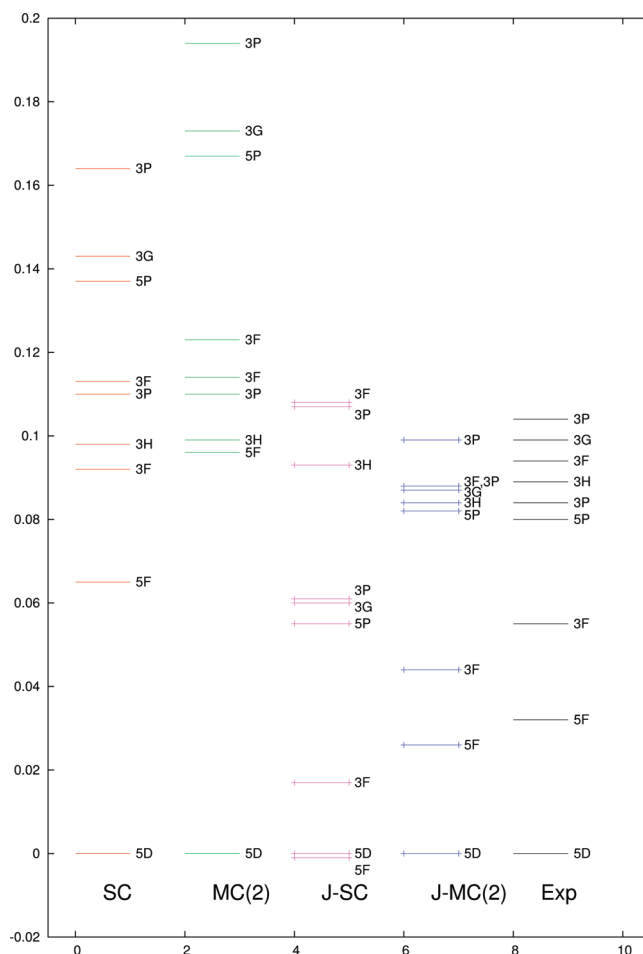

Figure 1. Some terms in atomic units of the low-lying spectrum of the iron atom obtained from the different trial wave functions studied in this work as compared with the experimental results[1] with the spin−orbit splitting averaged.

Finally, it is worth mentioning here the role that relativity plays on the excitation energies here studied. Relativity is present in the experimental values, whereas it has not been considered here. To estimate the relativistic correction to the present results, it is important to take into account first the important dependence of relativity on the state under study and second the strong interplay between relativity and correlations for the first-row transition-metal atoms.[17] For example, it has been obtained that relativity is more important for the states from the $3d^n4s^2$ configuration than for those from the $3d^{n+1}4s$ configuration in such a way that the relativistic excitation energy of the first excited state is larger than its nonrelativistic counterpart.[18] With respect to the dependence of the relativistic correction on the approximation employed to describe the state, a 15−30% reduction has been obtained in the relativistic correction when near degeneracy is included to describe the states from the $3d^n4s^2$ with respect to a Dirac Hartree−Fock calculation.[19] For example, the relativistic correction for the first excited state of the Fe atom in a single configuration approach is 0.01 and 0.008 au when a two-configuration wave function is employed[19] in the relativistic self-consistent field calculation.

Although the relativistic correction was obtained without using a Jastrow factor, if we simply add these values to the J-SC and J-MC(2) excitation energies obtained in this work, (−0.001(4) and 0.026(4) au, respectively), the result is 0.009(4) and 0.034(4) au, to be compared in the latter case with 0.032 au, that is, the experimental excitation energy of the first ^5F

excited state. Therefore, the J-MC(2) excitation energy with this approximate perturbative relativistic correction is in a good agreement with the experimental value. A similar situation can be expected for other states from the $3d^74s$ configuration, although the exact value of the correction could be different from that of the first excited state. Although a calculation with the explicitly correlated wave function of this work may provide different values for the relativistic correction to the excitation energy, both the sign and the order of magnitude of the correction is expected to be qualitatively correct.

Conclusions

An all-electron Variational Monte Carlo calculation for the ground state and for the lowest energy LS states of the ground-state configuration of the iron atom has been carried out. Explicitly correlated wave functions including near degeneracy effects are obtained. The importance of the correlation mechanisms included has been systematically analyzed for these excited states.

The effect of 4s−4p near degeneracy on explicitly correlated wave functions is to reduce the energy between 0.03 and 0.04 hartree with respect to a single configuration calculation for all states from the ground-state configuration. Therefore, the improvement on the excitation energy of these terms provided by the two- configuration explicitly correlated wave functions with respect to the single configuration explicitly correlated wave functions is very small.

Because the states from the $3d^74s$ configuration do not present near degeneracy effect, the excitation energy of these states is increased by ∼0.03 hartree when near degeneracy is included in the ground state. This leads to a much better comparison with the experimental excitation energies.

Relativistic corrections have been included in an approximate way by obtaining a better comparison with the experimental values. To refine the comparison, relativistic effects need to be considered simultaneously with the different correlation mech-anisms considered in the wave function. Similar conclusions have been raised in other works employing different methodologies.

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