Correlated wave functions for the ground and some excited states of the iron atom

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We study the states arising from the [Ar]4s²3d⁶ and [Ar]4s³3d⁷ configurations of iron atom with explicitly correlated wave functions. The variational wave function is the product of the Jastrow correlation factor times a model function obtained within the parametrized optimized effective potential framework. A systematic analysis of the dependence of both the effective potential and the correlation factor on the configuration and on the term is carried out. The ground state of both, the cation, Fe⁺, and anion, Fe⁻, are calculated with correlated wave functions and the ionization potential and the electron affinity are obtained. © 2006 American Institute of Physics. [DOI: 10.1063/1.2192504]

I. INTRODUCTION

Explicitly correlated wave functions constitute a suitable variational ansatz for describing atomic bound states. Dynamic correlations among the electrons are described by means of the Jastrow factor while both mean field effects and the antisymmetry of the total wave function are taken into account by means of a model wave function which is written as a linear combination of a few Slater determinants. This model wave function also provides the angular momentum quantum numbers of the state under study. The use of the Jastrow factor reduces drastically the number of Slater determinants in the expansion. The major drawback of this kind of trial wave functions lies in the calculation of the expectation value of the different operators. This problem, however, can be overcome by using Monte Carlo-type quadratures that provide the required accuracy for dealing with these wave functions in atomic structure calculations. The variational Monte Carlo (VMC) method allows one to deal with very general forms of the trial wave function, in such a way that it has become a powerful tool in quantum chemistry calculations.

The use of a well tailored correlation factor is necessary to obtain accurate results, but for some systems this is not sufficient. There are important effects that are hard to describe in the correlation factor and they are better accounted in the model wave function. The optimized effective potential (OEP) method in its parameterized version [parametrized optimized effective potential (POEP)] has shown to be an appropriate framework to obtain the single particle orbitals, and then the model wave function. The trial wave functions obtained within this scheme are very efficient in the description of the ground and low-lying excited states of some light atoms and ions. For those states, and using these correlated trial wave functions, more than 90% of the correlation energy is recovered. Finally, it is worth mentioning that, once the wave function is obtained, the Monte Carlo quadrature can be used to obtain some other properties of interest such as the one- and two-body densities and their radial moments.

The generalization of this ansatz to heavier atoms is, in principle, straightforward with the only cost of increasing the computing time. In spite of that not many studies for N > 18 atoms have been found in the literature. In most of them, a pseudopotential has been used in order to account for the inner core electrons. These approximations provide a good estimation of the energy differences between the states although they do not allow for the calculation of the total energy of the term. Nowadays it is possible to compute the total energy in an all electron calculation of the ground and low-lying excited states of medium weight atoms 18 ≤ N ≤ 36 with an accuracy of mhartree by using explicitly correlated wave functions as it was done for the lighter atoms.

The transition elements constitute the most appropriate playground to carry out the study with the explicitly correlated wave functions built from a POEP model wave function. Accurate calculations of these elements are hard to achieve because of the special features of their electronic structure, see, e.g., Ref. 14. For these atoms both the ground state and the closest in energy configurations present a high term multiplicity, especially for the case of a nearly half-filled 3d subshell. For example, the ground state of the Fe atom is a 5D term arising from the configuration [Ar]3d⁶4s², whereas the first excited state is a 5F term coming from the [Ar]3d⁷4s configuration. Some of the terms coming from any of these two configurations cover most part of the low energy spectrum of iron atom, while some others lie above...
the ionization threshold. In this work we will study the states of the iron atom arising from these two configurations by using a trial wave function with POEP orbitals and the Jastrow factor. We shall focus on the dependence of the excitation energy on the configuration, and on the dependence of the correlation factor on both the term and the configuration. It is worth to point out here that the use of these correlated wave functions leads to a better comparison with the experimental excitation energies.\(^{16}\) Atomic units are used throughout unless otherwise indicated.

II. WAVE FUNCTION

The correlated trial wave function, \(\Psi\), used in this work is the product of a symmetric correlation factor, \(F\), which includes the dynamic correlation among the electrons, times a model wave function, \(\Phi\), that provides the correct properties of the exact wave function such as the spin and the electronic coordinates.

\[
\Psi = F \Phi.
\] (1)

For the correlation factor we use the form of Boys and Handy\(^{2}\) with the prescription proposed by Schmidt and Moskowitz.\(^{3}\)

\[
F = e^{\sum_i c_i U_{ij}},
\] (2)

and

\[
U_{ij} = \sum_{k=1}^{N_e} \sum_{l=1}^{N_e} c_k (\tilde{r}_i^{m_k} \tilde{r}_j^{n_k} + \tilde{r}_i^{n_k} \tilde{r}_j^{m_k}) \tilde{r}_{ij}^{q_k},
\] (3)

where

\[
\tilde{r}_i = \frac{b r_i}{1 + b r_i}, \quad \tilde{r}_{ij} = \frac{b r_{ij} + 1}{d r_{ij}}.
\]

The coefficients \(b\) and \(d\) represent the inverse of the effective range of the correlation which have been fixed at the value of one atomic unit in the present calculation, and \(c_k\) are the variational parameters. We have worked with \(N_e=17\), including electron-nucleus, electron-electron, and electron-electron-nucleus correlations. The first coefficient is fixed to satisfy the electron-electron cusp exactly while the others are taken as variational parameters.

The model wave function is obtained within the POEP framework. For any of the nondegenerate terms arising from the configurations considered, the model wave function is built as a single term and is written as a linear combination of Slater determinants with the proper values of the total spin and orbital angular momentum of the term under study. There also appear twofold degenerate terms from these configurations. For them we have diagonalized the Hamiltonian in the corresponding subspace.

The orbitals \(\phi_\mu\) in the model wave function \(\Phi\) are obtained by using the OEP approximation, by solving the Schrödinger equation

\[
(-\frac{1}{2} \nabla^2 + V(r)) \phi_\mu(r) = \epsilon_\mu \phi_\mu(r),
\] (4)

where \(V(r)\) is the optimized effective potential. In the parametrized version of the OEP method here applied, the effective potential is written as

\[
V(r) = -\frac{1}{r} [Z - N + 1 + (N - 1) f(r)],
\] (5)

where \(Z\) is the nuclear charge, \(N\) is the number of electrons, and

\[
f(r) = \sum_{p=0}^{s} \sum_{k=1}^{n_p} d_{k,p} r^p e^{-\theta_k r^p}.
\]

This expansion presents the proper asymptotic behavior at both large \(r\) values and short electron-nucleus distances if the following constraint on the parameters is imposed

\[
\sum_{k=1}^{n_0} d_{k,0} = 1.
\]

The parameters of the potential are fixed by minimizing the expectation value of the Hamiltonian with some additional constraints.\(^{7}\) The first one is the fulfillment of the virial theorem. The second one is that the exchange-only virial relation\(^{17,18}\) must hold. This theorem states that the exchange energy defined in the usual way

\[
E_x = -\frac{1}{2} \sum_{\mu \nu} \langle \phi_\mu \phi_\nu \frac{1}{r_{12}} | \phi_\nu \phi_\mu \rangle,
\]

must be equal to

\[
E_x^r = -\int d\rho(r) \mathbf{r} \cdot \nabla V_x(r),
\]

where \(V_x(r)\) is the exchange potential

\[
V_x(r) = V(r) - \left[ -\frac{Z}{r} + \sum_\mu \int d\rho_2 |\phi_\mu(r_2)|^2 \right].
\]

All the sums run over the occupied orbitals. The third constraint concerns to the occupied orbital with the highest eigenvalue in Eq. (4). The eigenvalue associated to this orbital, must be equal to the following expectation value\(^{19}\)

\[
\bar{\epsilon}_\lambda = I_\lambda + \sum_\mu (J_{\lambda \mu} - K_{\lambda \mu}),
\] (6)

where \(I, J,\) and \(K\) are the usual single particle, direct and exchange integrals calculated starting from the eigenfunctions of the effective potential. The energies \(\bar{\epsilon}_\lambda\) of Eq. (6) do not coincide with the eigenvalues \(\epsilon_\lambda\) of the corresponding single particle Schrödinger equation with the effective potential (5), except for the highest occupied orbital.\(^{19}\) The parametrized optimized effective potential approach provides results very close to the Hartree-Fock ones for the atomic ground states\(^{8}\) with relative energy differences below 0.001%.

Once the model wave function is fixed within the POEP framework, the Jastrow factor, \(F\), is introduced and the total
energy of the term is minimized with respect to the free parameters of $F$, i.e., with respect to the $c_k$ coefficients in Eq. (3).

III. RESULTS

A. Noncorrelated results

The POEP method has shown to be an excellent approximation to the Hartree-Fock one for the ground state. No previous study on the performance of the POEP for the low-lying excited states of iron has been found in the literature. It is worth to remark here that the POEP approximation is basing, as the Hartree-Fock (HF) one, on the variational principle with a mean field trial wave function. Therefore the POEP energy must be an upper bound to the HF one. A comparison, where available, of the HF and POEP energies is the most straightforward way of estimating the efficiency of the POEP method. Besides, it can be useful to study the structure of the effective potential function, focusing mainly on its dependence on the term and configuration.

In Table I we report the total energy as well as the single-particle energies of both the $^5D$ ground state and the $^5F$ first excited state of the Fe atom obtained with the POEP method as compared with the corresponding Hartree-Fock energies. The analytical form of both the single particle orbitals and the effective potential have been taken to be the same for both states within the POEP method. The optimization leads to a different set of optimum parameters.

The difference between the total energy from the HF and POEP methods is smaller than $1$ in $10^6$ for both states. With respect to the single particle energies, the relative difference between the POEP and the HF values is slightly higher for the $^5F$ state, but always below $0.8\%$. The highest relative differences are found for the $4s$ state, the least bound one.

The effective potential is very similar for both states. In Fig. 1 we plot the $f(r)$ function that gives the effective potential, see Eq. (5), for the two terms here studied. The difference function multiplied by 100 (to fit the scale) is also shown.

It is apparent from this figure the small difference between these two functions, below $1\%$ in the interval shown. To better elucidate the importance of this difference in the effective potential the following calculation has been performed. By using the optimum potential obtained for the ground $^5D$ term, a calculation for the $^5F$ has been carried out. In such calculation the effective potential is kept fixed so that the total energy has been minimized only with respect to the parameters of the single particle orbitals. The energy obtained in this way is $E=-1262.25295\ h$, i.e., $0.12\ h$ above the full POEP optimization for the $^5F$ term (see Table I). This difference is almost twice the excitation energy at the HF or POEP levels. Because these two terms come from two different electronic configurations, it can be concluded that the effective potential presents a non-negligible dependence on the configuration, at least for the total energy.

A study of all the states arising from the configurations $[\text{Ar}]3d^64s^2$ and $[\text{Ar}]3d^64s^1$ is carried out in Tables II and III, respectively. In Table II we report the results for the states effective potential.

\begin{table}[h]
\centering
\begin{tabular}{|l|c|c|c|}
\hline
Term & $E_{\text{HF}}$ & $[V(r) - V^5D]$ & $[V(r) - V^5F]$ \\
\hline
$^5D$ & $-1262.4432$ & $-1262.43632$ & $-1262.43632$ \\
$^3H$ & $-1262.3437$ & $-1262.33690$ & $-1262.33781$ \\
$^1P$ & $-1262.2514$ & $-1262.23259$ & $-1262.23259$ \\
$^1F$ & $-1262.2514$ & $-1262.23221$ & $-1262.23313$ \\
$^3G$ & $-1262.3173$ & $-1262.31036$ & $-1262.31137$ \\
$^1S$ & $-1262.2805$ & $-1262.27320$ & $-1262.27470$ \\
$^1D$ & $-1262.0871$ & $-1262.25289$ & $-1262.25473$ \\
$^1F$ & $-1262.1399$ & $-1262.23936$ & $-1262.24122$ \\
$^2F$ & $-1262.2156$ & $-1262.24257$ & $-1262.24073$ \\
$^2P$ & $-1262.1674$ & $-1262.16850$ & $-1262.1650$ \\
$^2G$ & $-1262.13037$ & $-1262.13384$ & $-1262.13584$ \\
$^2D$ & $-1262.02157$ & $-1262.02718$ & $-1262.02718$ \\
$^2S$ & $-1261.89967$ & $-1261.90666$ & $-1261.90666$ \\
\hline
\end{tabular}
\end{table}

FIG. 1. $f(r)$ functions of the effective potential, Eq. (5) for the two terms $[\text{Ar}]3d^64s^2$ and $[\text{Ar}]3d^64s^1$, of the Fe atom and the difference function between them multiplied by 100.

TABLE II. Total energy for the different terms of the ground state configuration, $[\text{Ar}]3d^64s^2$ of the iron atom obtained within the HF framework (Ref. 20) and by using two different parametrizations of the effective potential: $[V(r) - V^D]$ is that optimized for the $^D$ term and $[V(r) - V^\text{opt}]$ is optimized for each term. The states below the $^1D$ one, except the $^1P$ one, are experimentally above the ionization threshold.
TABLE III. Energy of the different terms from the [Ar]3d⁶4s configuration of the iron atom obtained by using different options for the effective potential. For the lowest energy term from this configuration, 3F, the Hartree-Fock energy is $E = -1262.3763 \ h$. The states below the horizontal line are experimentally above the ionization threshold.

<table>
<thead>
<tr>
<th>Term</th>
<th>$[V(r)−5D]$</th>
<th>$[V(r)−1F]$</th>
<th>$[V(r)−opt]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3F$</td>
<td>−1262.252 95</td>
<td>−1262.370 51</td>
<td>−1262.370 51</td>
</tr>
<tr>
<td>$1^3F$</td>
<td>−1262.224 24</td>
<td>−1262.342 24</td>
<td>−1262.343 75</td>
</tr>
<tr>
<td>$3P$</td>
<td>−1262.173 53</td>
<td>−1262.298 41</td>
<td>−1262.299 64</td>
</tr>
<tr>
<td>$3G$</td>
<td>−1262.166 10</td>
<td>−1262.291 70</td>
<td>−1262.293 45</td>
</tr>
<tr>
<td>$1G$</td>
<td>−1262.151 75</td>
<td>−1262.277 56</td>
<td>−1262.279 27</td>
</tr>
<tr>
<td>$1^3P$</td>
<td>−1262.144 82</td>
<td>−1262.270 14</td>
<td>−1262.272 21</td>
</tr>
<tr>
<td>$3H$</td>
<td>−1262.139 63</td>
<td>−1262.267 67</td>
<td>−1262.269 60</td>
</tr>
<tr>
<td>$2^3P$</td>
<td>−1262.130 89</td>
<td>−1262.267 66</td>
<td>−1262.269 36</td>
</tr>
<tr>
<td>$1^3D$</td>
<td>−1262.130 46</td>
<td>−1262.259 52</td>
<td>−1262.261 43</td>
</tr>
<tr>
<td>$3^3H$</td>
<td>−1262.125 27</td>
<td>−1262.253 53</td>
<td>−1262.255 38</td>
</tr>
<tr>
<td>$1^3P$</td>
<td>−1262.125 27</td>
<td>−1262.253 53</td>
<td>−1262.255 38</td>
</tr>
<tr>
<td>$1^3D$</td>
<td>−1262.116 11</td>
<td>−1262.245 39</td>
<td>−1262.247 19</td>
</tr>
<tr>
<td>$2^3F$</td>
<td>−1262.051 26</td>
<td>−1262.195 57</td>
<td>−1262.197 90</td>
</tr>
<tr>
<td>$1^1F$</td>
<td>−1262.045 86</td>
<td>−1262.181 44</td>
<td>−1262.184 21</td>
</tr>
<tr>
<td>$2^1D$</td>
<td>−1262.046 93</td>
<td>−1262.100 05</td>
<td>−1262.105 08</td>
</tr>
<tr>
<td>$2^3D$</td>
<td>−1261.930 71</td>
<td>−1262.085 91</td>
<td>−1262.090 65</td>
</tr>
</tbody>
</table>

arising from the [Ar]3d⁶4s² ground state configuration. The HF results of Clementi and Roetti are also reported for the sake of comparison. For the degenerate terms, the HF results correspond to the Slater average and have been not written for the second term.

The results shown in the $[V(r)−opt]$ column have been obtained by optimizing the free parameters of the potential with respect to the energy of each term. On the other hand, the $[V(r)−5D]$ results are obtained by using the optimized effective potential and the single particle orbitals corresponding to the $3D$ term. Therefore, for this second set of results no variational freedom is considered. The energy differences are very small, about 1 mh, for all of the bound states, much smaller than the differences between Hartree-Fock and the best POEP energy. The difference increases slightly for the unbound states, especially for the second term of the degenerate states. This result indicates that, within a given configuration, the optimized effective potential is nearly independent of the term, especially if they are close in energy.

A similar analysis is performed in Table III for the [Ar]3d⁶4s configuration. In this case we have carried out three sets of calculations.

The first one, given in the column $[V(r)−opt]$, consists in a full minimization of the total energy, optimizing all of the free parameters, i.e., those in the effective potential and those of the single particle orbitals. The results shown in the column $[V(r)−1F]$ have been obtained by using both the effective potential and the radial single particle functions optimized for the [Ar]3d⁶4s 1F term, i.e., the lowest energy term of that configuration. Finally, in column $[V(r)−3D]$ we quote the expectation value of the energy of the corresponding term calculated with the orbitals optimized for the ground state. As it is apparent from the results, when a different configuration is used to fix the orbitals, the total energy is quite different to the optimal one. However, if the orbitals are taken from a different term of the same configuration, the total energy is very close to the most accurate one. The trend for the different terms is similar to that of the other configuration. Therefore one can conclude that, within a given configuration, the use of the parameters optimized for the lowest energy term to calculate the total energy of a different one does not introduce a significant penalty. This does not happen if the terms correspond to different configurations.

B. Correlated results

When the Jastrow factor is included in the variational ansatz the calculations have been performed by using the variational Monte Carlo method. The results thus obtained are labelled as JPOEP. The optimization of the free parameters in the Jastrow factor can be a time consuming procedure. Therefore we have performed a previous study on the dependence of the correlation factor on both the configuration and the term studied in order to test the accuracy of using a common correlation factor for different terms from a given configuration. Thus, for the [Ar]3d⁶4s² ground state configuration we have found that the energy obtained for both the $1^3H$ and $1^3P$ terms when the ground state correlation factor is employed is very close to the corresponding ones obtained after a full optimization of the correlation factor. In particular, an energy difference between both calculations of about 10 mh is found. This constitutes approximately 1% of the correlation energy recovered with the full optimization.

For states coming from different configurations the situation is different when a similar comparison is performed. For example, if the Jastrow factor of the ground state is employed for the [Ar]3d⁶4s 1F term the total energy obtained is $−1263.3415(18)$ to be compared with the energy obtained from a full minimization of the correlation factor that is $−1263.3771(17)$. We see that the energy difference is three times larger than before. This represents a little bit more than 5% of the correlation energy of this term. Although this difference may appear small, its magnitude is important and can have effects on the energy ordering of the terms. Therefore we shall use for all of the terms of a given configuration the same correlation factor, that will be optimized for the lowest energy term of the configuration. In doing so we will miss some of the variational freedom of the problem, but the computer time will be strongly reduced and the penalty on the total energy will not be significant.

In Table IV we report the total energy for the terms coming from the configurations [Ar]3d⁶4s² and [Ar]3d⁶4s, obtained by using both noncorrelated (POEP) and correlated (JPOEP) wave functions.

The correlation energy here obtained for the ground state is more than 20% higher than that reported in Ref. 15. As it can be seen from the table, the correlation energy is almost independent of the term within a given configuration, but presents different values for the two different configurations. Thus in the configuration [Ar]3d⁶4s², the correlation energy takes values between 0.93 and 0.97 h while in the [Ar]3d⁶4s one the correlation energy oscillates around 1.02 h, and is a bit greater for the unbound states. When comparing both
configurations, some experimental results are not well reproduced. For example, the energy difference between the $^2D$ and $^5F$ terms is 0.06 a.u. in the Hartree-Fock approximation. When correlations are introduced, the energies become closer in such a way that they cannot be distinguished due to the statistical error. The experimental separation energy for these two states is 0.03 a.u. Therefore, correlations give the correct trend but the correction is too big to reproduce the experimental value. Some effect that must improve these results are the consideration of both configuration mixing in the model wave function to account for some nondynamic correlations, and relativistic corrections in the electronic Hamiltonian in order to better fit the experimental excitation energies.

In Table V we report the excitation energy with respect to their corresponding $^2D$ ground state of the experimental bound states calculated within both the POEP and the correlated JPOEP frameworks as compared with the experimental ones of Ref. 16. For any of the experimental states we have

| Term | $^2D$ | $^5F$ | $^5F$ | $^3p$ | $^1p$ | $^1p$ | $^3F$ | $^3F$ | $^3G$ | $^3p$ | $^1G$ | $^1D$ | $^1D$ | $^3F$ |
|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| POEP | 0.0  | 0.065| 0.027| 0.137| 0.113| 0.125| 0.168| 0.157| 0.167| 0.175| 0.181| 0.189| 0.181|
| JPOEP| 0.0  | 0.001| 0.017| 0.055| 0.108| 0.060| 0.083| 0.078| 0.083| 0.097| 0.096| 0.097| 0.092|
| Expt. | 0.0  | 0.032| 0.055| 0.080| 0.084| 0.089| 0.099| 0.112| 0.119| 0.119| 0.125| 0.130| 0.131|

TABLE IV. Noncorrelated, $E_{POEP}$, and correlated, $E_{JPOEP}$, total energy for the terms of the two configurations $[\text{Ar}]3d^64s^2$ and $[\text{Ar}]3d^64s^1$ of the iron atom. In parentheses we give the statistical error in the last figures.
TABLE VI. Ground state energy of the neutral iron atom, its cation and its anion obtained by using the HF method, \( E_{\text{HF}} \), the POEP approximation, \( E_{\text{POEP}} \), and the correlated wave function of this work, \( E_{\text{POEP}} \). The relativistic corrections to the total energy of the cation and the neutral atom obtained within a HF framework, \( \Delta E_{\text{RHF}} \), of Ref. 21 and the corresponding correction to the ionization potential are also shown. The ionization potential \( I = E(\text{Fe}^+) - E(\text{Fe}) \) and the electron affinity \( A = E(\text{Fe}^+) - E(\text{Fe}^-) \) are given in eV. The experimental ionization potential is \( I_{\text{exp}} = 7.9024 \text{ eV} \),\(^{16} \) and the experimental electron affinity is \( A_{\text{exp}} = 0.151(3) \text{ eV} \) (Ref. 22).

<table>
<thead>
<tr>
<th>( \text{Fe}^+ )</th>
<th>( E_{\text{HF}} )</th>
<th>( E_{\text{POEP}} )</th>
<th>( E_{\text{POEP}} )</th>
<th>( \Delta E_{\text{RHF}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>−1262.2130</td>
<td>−1262.1989</td>
<td>−1263.0997(9)</td>
<td>−8.526791</td>
</tr>
<tr>
<td>Fe</td>
<td>−1262.4432</td>
<td>−1262.4363</td>
<td>−1263.3757(19)</td>
<td>−8.597770</td>
</tr>
<tr>
<td>Fe</td>
<td>−1262.3671</td>
<td>−1262.3491</td>
<td>−1263.3717(14)</td>
<td>−8.597770</td>
</tr>
</tbody>
</table>

\( I \) (eV) | 6.27 | 6.46 | 7.51(8) | 0.35
\( A \) (eV) | −2.07 | −2.37 | −0.11(9) |

reported the energy corresponding to the most bound term in each total angular momentum multiplet. As can be seen for the states from the 3d\(^4\)4s\(^2\) configuration the ordering of the different calculated states coincides with the experimental ones except the 1 \(^3\)P and the 3 \(^3\)H which are interchanged. The same happens with the last excited state which experimentally is the 1 \(^3\)D one, although, in our calculation, the 1 \(^1\)S state is more bound than the 1 \(^1\)D one. In addition the POEP excitation energies are slightly greater than the corresponding JPOEP ones, which approach more to the experimental results.

For the states from the 3d\(^4\)4s\(^1\) configuration, correlations leads, in general, to a better agreement with the experimental result,\(^{16} \) despite some of the states cannot be separated in energy due to the statistical error in the Monte Carlo calculation. Besides the difference between the correlated and the experimental excitation energies for these states is nearly independent of the state, and oscillates between 0.03 and 0.04 h. This difference could be mainly due to the near degeneracy 4s-4p effect which has not been considered in the present calculation for the states from the 3d\(^4\)4s\(^2\) configuration. For example, within the POEP approximation the ground state energy decreases from −1262.4363 up to −1262.4666 h when the 4s-4p near degeneracy is considered, i.e., a decrease of −0.030 h, although this difference could be different in a correlated calculation.

The electronic correlations are important for the ionization potential and the electron affinity of the iron atom. In Table VI we show the energies obtained from the HF method, the POEP approximation and the correlated wave functions. The different correlation factors for all of the terms in a given configuration leads to inaccuracies on the correlation energy below 1%. If a correlation factor optimized for a different configuration is employed, the differences on the correlation energy rise up to 3%, which may lead to a different energetic ordering of the terms. Electronic correlations, although improve the results with respect to HF or POEP, are not enough to not reproduce the experimental energetic ordering of the terms. The inclusion of relativistic corrections along with the correlated wave functions of this work is expected to give a quite accurate agreement between theory and experiment. A crude estimation of the relativistic effects gives for the ionization potential a result that compares very well with the experimental value.

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Atomic Spectra Database. Version 2.0, National Institute of Standards and Technology (1999); http://physics.nist.gov/cgi-bin/AtData/main_asd