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Density functional theory calculations of one electron Rydberg states in Li atom

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Summary. It is shown by comparison with the available time-dependent coupled Hartree–Fock calculations that the self-interaction-corrected local-spin-density functional theory, with correlation energy, provides an accurate description of the transition energy and the radial expectation values $\langle R^{-1}\rangle$ and $\langle R\rangle$, for the Rydberg states ($n=2$–8) of Li($1s^2nl^1$) atom. A simple criterion is proposed to define the percentage of Rydberg character of a valence *ns* orbital.

Key words: Rydberg states — Atomic Li — Density functional theory

It is well known that an exact treatment of the self-interaction potential within $X\alpha$-theory [1] leads to a significantly improved description of the various atomic properties [2–6]. Similarly, the self-interaction-corrected local-spin-density (SIC-LSD) approximation with correlation energy has been successfully tested to predict electron affinities of neutral atoms [7–9]. In a recent paper [10] the SIC-LSD calculations of dipole matrix elements have been performed on the Rydberg states of the oxygen atom in the quintet and triplet manifolds, respectively, and the results have been found to be in excellent agreement with the corresponding Hartree–Fock results. Since the simplified representation of correlation effects is an attractive feature of the SIC-LSD functional theory it would be useful to compare the results of such calculations with a suitable post HF level of calculations which include correlation effects derived from the wave function approach. In this communication we have examined the doublet Rydberg levels of Li within the quasi-relativistic SIC-LSD scheme, with correlation energy, as developed by Perdew and coworkers [7]. In particular, we compare the transition energy, ΔE, and radial expectation values $\langle R^{-1}\rangle$ and $\langle R\rangle$ with the available time-dependent coupled Hartree–Fock (TDCHF) calculations [11]

Table 1. A comparison of the radial expectation value $\langle R^{-1} \rangle$ and $\langle R \rangle$ as calculated using the SIC-LSD approximation for the one electron Rydberg states of Li with the TDCHF results. Similar comparison of the transition energy, ΔE, along with the experimental value [13] are given in the last three columns. All values are in a.u.

Transition	$\langle R^{-1} \rangle$		$\langle R \rangle$		ΔE			
	SIC-LSD	TDCHF	SIC-LSD	TDCHF	Expt.	SIC-LSD	LSD	TDCHF
$2s \rightarrow 2p$	1.8855	1.8787	1.909	1.974	0.0679	0.0645	0.0667	0.0671
$2s \rightarrow 3s$	1.8409	1.8362	3.719	3.798	0.1240	0.1238	0.1198	0.1239
$2s \rightarrow 3p$	1.8348	1.8284	4.270	4.451	0.1409	0.1399	0.1359	0.1394
$2s \rightarrow 3d$	1.8321	1.8271	3.867	3.877	0.1426	0.1440	0.1433	0.1407
$2s \rightarrow 4s$	1.8195	1.8144	6.751	6.895	0.1595	0.1601	0.1572	0.1597
$2s \rightarrow 4p$	1.8172	1.8114	7.582	7.954	0.1662	0.1663	0.1630	0.1645
$2s \rightarrow 4d$	1.8158	1.8109	7.356	7.369	0.1669	0.1683	0.1658	0.1650
$2s \rightarrow 4f$	1.8157	1.8110	6.380	6.359	0.1669	0.1684	0.1668	0.1650
$2s \rightarrow 5s$	1.8104	1.8049	10.641	11.117	0.1745	0.1755	0.1731	0.1747
$2s \rightarrow 5p$	1.8093	—	11.727	—	0.1778	0.1785	0.1762	0.1779
$2s \rightarrow 5d$	1.8084	1.8035	11.746	11.845	0.1781	0.1796	0.1776	0.1763
$2s \rightarrow 5f$	1.8083	1.8034	10.829	10.878	0.1782	0.1797	0.1779	0.1763
$2s \rightarrow 5g$	1.8083	—	9.510	—	—	0.1797	0.1782	—
$2s \rightarrow 6s$	1.8056	1.7998	15.397	16.459	0.1822	0.1835	0.1818	0.1819
$2s \rightarrow 6p$	1.8054	—	16.234	—	0.1840	0.1853	0.1835	0.1840
$2s \rightarrow 6d$	1.8050	—	16.155	—	0.1843	0.1860	0.1840	0.1842
$2s \rightarrow 6f$	1.8047	1.7993	15.536	16.538	0.1843	0.1860	0.1841	—
$2s \rightarrow 6g$	1.8042	—	14.925	—	—	0.1858	0.1845	—
$2s \rightarrow 6h$	1.8042	—	13.374	—	—	0.1858	0.1845	—
$2s \rightarrow 7s$	1.8036	1.7959	19.087	25.451	0.1867	0.1880	0.1870	0.1860
$2s \rightarrow 7p$	1.8027	—	21.353	—	0.1878	0.1879	0.1881	0.1878
$2s \rightarrow 7d$	1.8020	—	22.665	—	0.1879	0.1867	0.1883	0.1878
$2s \rightarrow 7f$	1.8015	—	22.917	—	0.1880	0.1867	0.1884	—
$2s \rightarrow 7g$	1.8021	—	20.416	—	—	0.1895	0.1885	—
$2s \rightarrow 7h$	1.8041	—	13.457	—	—	0.1895	0.1886	—
$2s \rightarrow 8s$	1.8019	1.7936	23.365	—	0.1895	0.1910	0.1907	—

which include certain classes of correlation effects [12]. Our theoretical ΔE values are also compared with the experimental results [13]. Finally, we propose a simple criterion to define the percentage of Rydberg character of the valence ns^1 orbital. We have considered the one electron excitations defined by $n = 3-8$ for the $\mathrm{Li}(1s^2nl^1)$ atom.

In Table 1, we have listed the results of our calculations. The SIC-LSD estimates of ΔE, $\langle R^{-1}\rangle$ and $\langle R\rangle$ are in excellent agreement with the TDCHF results except for highly excited ($n \geqslant 5$) levels. As pointed out earlier [14], this is probably due to an insufficient basis set being utilized to represent these states. The SIC-LSD ΔE values are in good agreement with the experimental values. With the inclusion of SIC therefore, the LSD theory can be used reliably to predict the valence excitations in atoms. It is important to mention here that without the SIC, the negative ion states do not lead to a convergent solutions. It is, however, possible to obtain pure LSD energies corresponding to neutral atomic excited states. The corresponding ΔE values are given in Table 1, column 8. They suggest that the SIC energy contributions of the two states cancel to a large extent. We define the percentage Rydberg character (PRC) of the valence ns-orbital as

$$\mathrm{PRC} = \frac{\langle r^{-1}\rangle\langle r\rangle}{1.5} \times 100, \tag{1}$$

where the radial expectation values refer to the valence orbital. For hydrogen atom, $\langle r^{-1}\rangle\langle r\rangle$ is 1.5. According to Eq. (1) the PRC for $\mathrm{Li}(ns^1)$ is calculated to be 96.0%, 97.1%, 97.7%, 98.1%, 98.4% and ~100%, respectively.

In summary, we have demonstrated the feasibility of using the SIC-LSD approximation with correlation energy to describe the Rydberg states of the lithium atom. The simple product $\langle r^{-1}\rangle\langle r\rangle$ for the valence ns orbital is compared with its hydrogenic value of 1.5 to define the percentage of Rydberg character of the ns-valence orbital.

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References

1. Slater JC (1972) Adv Quantum Chem 6:1
2. Sen KD, Weiss A (1979) Theor Chim Acta 52:181
3. Sen KD (1980) Chem Phys Lett 74:201
4. Maessen B, Schmidt PC (1981) Theor Chim Acta 59:299
5. Sawant VR, Kanhere DG (1984) J Phys B 17:3003
6. Gadre SR, Chakravoty S (1985) Chem Phys Lett 120:101
7. Cole LA, Perdew JP (1982) Phys Rev A 25:1965
8. Stoll H, Pavlidou CME, Preuss H (1978) Theor Chim Acta 49:143
9. Lagowski JB, Vosko SH (1988) J Phys B 21:203, for a recent comparison
10. Jackson KA, Lin CC (1989) Phys Rev B 39:1557, and references therein
11. Kundu, B, Mukherjee PK (1984) Theor Chim Acta 66:173; ibid (1969) 69:51
12. Caves TC, Karplus M (1969) J Chem Phys 50:3649
13. Bashkin S, Stoner JO Jr (1975) Atomic energy levels and Grotrian diagram, vol 1. Amsterdam, North-Holland; ibid (1978) p 27
14. Mukherjee PK, Ohtsuki K, Ohno K (1988) Theor Chim Acta 74:431