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A density functional investigation on the electronic and magnetic properties of LnSi (Ln=La-Lu) Diatom

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Abstract. Bond lengths, vibrational frequencies, electron affinities magnetic properties, and ionization potentials of the neutral and charged LnSi (Ln=La-Lu) diatom were studied by using the density functional method with relativistic effect being taken into account. Ground state was assigned for each species. The calculated natural populations of LnSi (Ln=La-Lu) exhibit that the charges are transferred mainly from $6s^2$ to $5d$, and most of $4f$ subshell in LnSi is inert without involving chemical bonding. The calculated highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gaps show that the HOMO-LUMO gaps are increased and exhibit oscillating behavior from LaSi to LuSi. Interestingly, total magnetic properties of LnSi (Ln =La-Lu)diatoms depend on the localized $4f$ electrons which generate the magnetic moment of LnSi diatoms; additionally, the magnetic moment of EuSi is 11 $\mu_{B,}$ which is the highest one. Comparisons with the available experimental and theoretical values are made and a good agreement is reached.

Keywords. Magnetic moment; geometries; electronic properties; HOMO-LUMO gaps; DFT.

1. Introduction

Transition metal capped silicon clusters have been studied extensively by using both theoretical and experimental methods because they may be employed not only as model systems for investigating localized effects in the condensed phase, but also as building blocks for developing new silicon based nanomaterials with tunable properties.[1–10] Rare earth lanthanides (Ln)-doped silicon are important material, this is because the Ln elements can retain significan portion of their magnetic moments even when they are enclosed by a silicon or germanium cage due to their localized f-electrons. Experimentally, Ohara *et al.* studied the $TbSi_n^-$ (n =6-16) clusters by using the photoelectron spectra (PES). Experimental results show that the Tb doped silicon clusters are relatively more stable towards photofragmentation than the bare silicon clusters of the same size.[2] The $LnSi_n^-$ (n =3-13, Ln=Ho, Gd, Pr, Sm, Eu, and Yb) clusters[5] are studied experimentally, and the dramatically increased adiabatic electron aff nities of $LnSi_n$clusters are found and attributed to their inherent electronic stabilization. Stimulated by the *experimental* measurements, several theoretical investigations on Ln-doped silicon clusters: $YbSi_n$(n =1-13), $EuSi_n$(n =1-13), $HoSi_n$,[10] and $LuSi_n$(n =1-12) clusters[6–9] have been performed.

In a way, rare earths are special transition metals possessing many of the properties, such as optical properties and magnetisms. Although there are some research studies on the properties of the Ln-doped silicon clusters, surely no systematic theoretical investigation on LnSi (Ln=La-Lu) diatoms has been reported so far. In order to understand the properties of the LnSi diatoms and provide some molecular parameters for future photoelectron mass experiments, a detailed study of the relative stabilities, structural and magnetic properties of LnSi diatoms is carried out taking relativistic effect into account.

In order to reveal the unusual properties of the rare earth Ln and silicon clusters, the main objective of this research, therefore, is to provide a detailed investigation of equilibrium geometries, charge-transfer properties, ionization potentials (IPs), electron affinitie (EAs), and HOMO-LUMO gaps of the LnSi diatoms. In addition, it should be pointed out that the relativistic effect of the

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rare earth LnSi is a challenging problem because of its complex $4f$ electrons.

2. Computational details

The explicit treatment of all the electrons in a cluster including rare earth element having a large number of atoms constitutes a demanding computational task. One of the best ways to surmount this difficult is to make use of relativistic electron core potentials (RECP), also known as relativistic pseudopotentials,[11] by means of which only the valence electrons are explicitly treated. RECP calculations can actually provide accurate results for both homo- and heteronuclear clusters bearing rare earth or silicon atoms and their various combinations as firml proven by previous investigations.[12] Therefore, the combination of density functional theory (DFT) methods with RECP's provides a feasible and accurate approach to the electronic structure study of the $LnSi^{0,\pm}$ (Ln =La-Lu) clusters as shown below.

Present calculations were done at the level of the density functional theory with the hybrid exchange and correlation (mPW3PBE) functional in combination with the 6-31G* basis sets for Si atom and Stuttgart quasi-relativistic effective core potentials (ECP28MWB) for La-Lu elements[11] as implemented in the Gaussian 09 code.[13] Geometry optimizations of LnSi (Ln =La-Lu) diatoms were systematically performed and were followed by the evaluation of their harmonic vibrational frequencies in order to attest the stability of the cluster. Spin-polarized calculations for the LnSi (Ln= La-Lu) diatoms were performed.

3. Results and Discussion

3.1 *Stabilities*

The calculated bond lengths, frequencies, total energies, IPs, and EAs of the neutral and charged LnSi (Ln=La-Lu) are tabulated in table 1. On the basis of the calculated results listed in table 1, it is found that the calculated Ln-Si bond lengths of the diatoms range from 2.4 Å to 3.0 Å, and the corresponding frequencies range from 210 cm^{-1} to 400 cm^{-1}.

The calculated La-Si bond length of LaSi diatom at the mPW3PBE level in combination with the 6-31G* basis sets for Si atom and ECP28MWB for La element is 2.44 Å, which is shorter than that at the B3LYP/LanL2DZ level (2.69 Å),[7] the calculated vibrational frequency is 404.3 cm^{-1}, which is higher than 335.8 cm^{-1} at the B3LYP/LanL2DZ level.[7] On the basis of our calculated results, one find that the relativistic effect influence the bond lengths and vibrational frequencies. The obtained electronic state of the doublet LaSi diatom is $^2\sum$. The calculated IP and EA are 5.94 and 0.67 eV, respectively. Furthermore, the calculated IP is larger than that (5.48 eV) obtained at the B3LYP/LanL2DZ level, however, our calculated EA is smaller than that (1.40 eV) at the same level of theory.[7] In addition, the magnetic moment of LaSi is computed to be 1.0 μ_B, which is in good agreement with that at the B3LYP/LanL2DZ level.[7] The calculated natural population of La in LaSi is 0.53, which deviates from that (0.25) at the B3LYP/LanL2DZ level.[7]

Table 1. Bond lengths for neutral (NL) and charged LnSi (**NL^+** and NL^-), the frequencies, IPs and EAs of LnSi (Ln=La-Lu).

Name	NL Å	Freq cm^{-1}	NL^+ Å	NL^- Å	IP eV	EA eV
LaSi	2.44	404.3	2.37	2.53	5.94	0.67
CeSi	2.53	362.1	2.51	2.65	5.49	0.15
PrSi	2.57	282.9	2.77	2.71	5.60	0.46
NdSi	2.90	231.1	2.48	3.04	6.27	0.89
PmSi	2.88	230.0	2.79	3.16	5.22	1.24
SmSi	2.89	229.6	3.08	3.04	6.30	0.94
EuSi	2.87	227.7	2.77	3.17	5.33	0.89
GdSi	2.48	335.2	2.47	2.60	6.13	0.04
TbSi	2.75	272.7	2.69	2.61	5.60	0.92
DySi	3.00	313.2	2.80	2.71	6.65	0.02
HoSi	2.84	218.8	3.57	2.85	6.77	0.08
ErSi	2.86	219.2	3.03	3.00	6.26	0.38
TmSi	2.84	220.3	2.72	2.86	5.57	0.93
YbSi	2.85	214.6	3.04	3.05	6.28	0.95
LuSi	2.67	276.4	2.63	2.86	6.52	0.01

CeSi diatom with different spin states is optimized; the most stable quintet CeSi isomer is obtained with electronic state of $^5\sum$. The calculated bond length and frequency of the neutral quintet CeSi diatom are respective 2.53 Å and 362.1 cm^{-1}. The calculated Ce-Si bond lengths of the negative and positive CeSi diatom are 2.65 and 2.51 Å, respectively. The Ce-Si bond length of the negative CeSi is longer than those of the neutral and positive diatoms, and the calculated bond length of the neutral one is longer than that of the positive diatom. The IP and EA are calculated to be, respectively, 5.49 and 0.15 eV.

As far as the PrSi diatom is concerned, the PrSi diatom with sextet spin state is optimized to be the most stable state with electronic state being $^6\sum$. The calculated Pr-Si bond length and frequency of the most stable PrSi diatom are respectively 2.57 Å and 282.9 cm^{-1}. The calculated Pr-Si bond lengths in the most stable charged PrSi clusters are 2.77 and 2.71 Å, respectively.

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from vertical ionization potential (VIP) result (5.5 eV) at the PW91 level,[6] and the EA is identical to the calculated adiabatic electron affinit (AEA).[6] In addition, the calculated HOMO-LUMO gap of EuSi is 2.84 eV, which is bigger than that (1.2 eV) at the PW91 level.[6] The atomic electronic charge of Eu in EuSi diatom is 0.25,[6] which deviates from our calculated result (0.55).

GdSi diatom is optimized at the mPW3PBE level. As seen from table 1, the frequency and bond length of the most stable GdSi with electronic spin state being S=5 are 335.2 cm^{-1} and 2.48 Å, respectively. Our calculated Gd-Si bond length of GdSi is shorter than 2.67 Å at the PW91 level.[15] The IP and EA of GdSi are respectively, 6.13 and 0.04 eV; moreover, the calculated IP of GdSi is consistent with the calculated VIP (6.00 eV) at the PW91 level.[15] The calculated total magnetic moment is 10 μ_B, which is slightly larger than that (9.44 μ_B) calculated at the PW91 level.[15] In addition, the calculated HOMO-LUMO gap of GdSi is 1.15 eV, which is larger than that (0.4 eV) at the PW91 level.[15] The atomic charge of Gd in GdSi diatom at the PW91 level is calculated to be 0.09,[15] which is smaller than our calculated value of 0.39.

TbSi diatom is computed by considering different spin states, the frequency and bond length of the most stable TbSi with electronic spin being S=7/2 are 272.7 cm^{-1} and 2.75 Å, respectively. The calculated Tb-Si bond length is shorter than that of $TbSi_{16}$ cluster (2.91-3.06 Å).[16] The calculated IP and EA results of TbSi are respectively, 5.60 and 0.92 eV.

DySi diatom is optimized and the calculated frequency and bond length of the most stable DySi with electronic spin being S=4 are 313.2 cm^{-1} and 3.00 Å, respectively. However, magnetic moment (8 μ_B) deviates from that *of* the Gd_3Si_4 crystal.[17] Furthermore, the Dy-Si bond length of DySi is in good agreement with those of Gd_3Si_4 crystal.[17] The IP and EA of DySi diatom are calculated to be 6.65 and 0.02 eV, respectively.

According to the calculated data of HoSi diatom, the frequency and bond length of HoSi with spin septet state are respectively, 218.8 cm^{-1} and 2.84 Å. Our calculated Ho-Si bond length is slightly longer than that (2.82 Å) calculated at the BW91 level;[10a] however, the calculated Ho-Si bond length is longer than that (2.73 Å) at the X3LYP level with ECP56MHF ECP for Ho atom and 6-31G basis sets for silicon atom.[10b] Furthermore, the obtained total magnetic moment is 6 μ_B, which is bigger than that at the BW91 level.[10a] The IP and EA are calculated to be are 6.77 and 0.08 eV, respectively.

On the basis of the calculated results of the ErSi diatom, the calculated Er-Si bond length and frequency of ErSi are 2.86 Å and 219.2 cm^{-1}, respectively. Our calculated Er-Si bond length in ErSi diatom is slightly shorter than the experimental result (3.09±0.04 Å) obtained by using Auger-electron diffraction (AED) and surface-extended x-ray-absorption fin structure (SEXASFS).[18] The calculated IP and EA values of ErSi diatom are 6.26 and 0.38 eV, respectively.

According to the calculated results of TmSi diatom, the calculated Tm-Si bond length and frequency of TmSi are respectively, 2.84 Å and 220.3 cm^{-1}. The most stable TmSi diatom is quintet spin state and its total magnetic moment is calculated to be 4μ_B. The bond lengths of negative and positive diatoms are calculated to be respectively, 2.86 and 2.72 Å In addition, the calculated IP and EA for TmSi are 5.57 and 0.93 eV, respectively.

As for the YbSi diatom, the calculated bond length and frequency of triplet YbSi are 2.85 Å and 214.6 cm^{-1}, respectively. The calculated Yb-Si bond length of the triplet YbSi is in good agreement with that at the GGA (BP) level with a frozen-core triple-ζ basis sets plus polarization function (TZP), a combined scalar or spin-orbit relativistic (SR) zeroth-order regular approximation (ZORA) being taken into account.[3] The calculated Yb-Si bond lengths of the charged YbSi are longer than that of the neutral one, indicating that the removal or addition of charge to the YbSi diatom will lead to an elongation of Yb-Si bond length, this findin is in good agreement with that at the GGA (BP) level with a frozen-core triple-ζ basis sets plus polarization function (TZP).[3] Furthermore, the calculated IP and EA of YbSi are 6.28 and 0.95 eV, respectively; the obtained IP and EA are in good agreement with the calculated IP (6.37 eV) and EA (1.05 eV) at the BP level with a frozen-core triple-ζ basis sets plus polarization function (TZP) and with the relativistic effect being considered, respectively.[3] In addition, the magnetic moment of YbSi is calculated to be 2 μ_B.

According to the calculated results of LuSi diatom, one find that the Lu-Si bond length and frequency are respectively, 2.67 Å and 276.4 cm^{-1}; which deviate slightly from the bond length and vibrational frequency (2.74 Å and 2570 cm^1) of the LuSi diatom obtained at the revised Perdew-Burke-Ernzerhof correlation functional (RPBE) level.[19] The bond length for the positive diatom is slightly shorter while the bond length for the negative diatom is longer than that of the neutral diatom. The calculated IP and EA of LuSi diatom are respectively, 6.52 and 0.01 eV. Furthermore, the calculated magnetic moment of LuSi is 2 μ_B.

On the basis of calculated IP and EA of LnSi diatom, the calculated IP values are generally larger indicating that all the LnSi diatoms are difficul to be ionized;

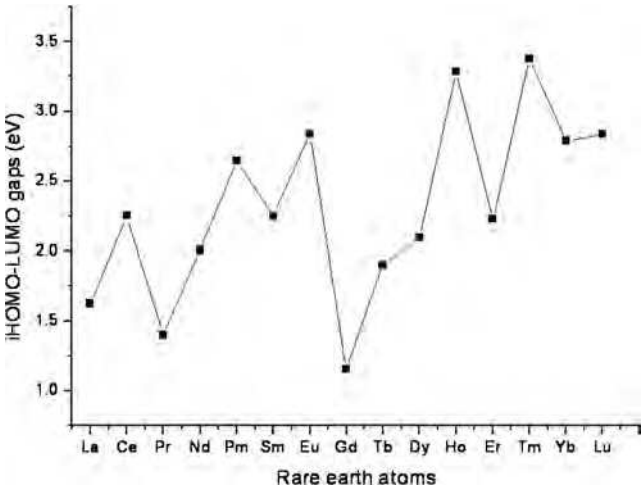

Figure 2. The HOMO-LUMO gaps of LnSi (Ln=La-Lu).

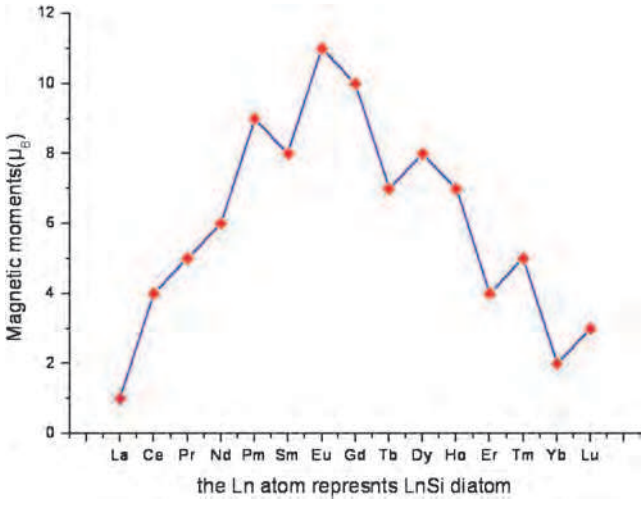

Figure 3. The total magnetic moments of LnSi (Ln=La-Lu).

HOMO-LUMO gaps than their neighboring diatoms while the GdSi has the smallest HOMO-LUMO gap of all LnSi diatoms, indicating that the GdSi is a soft molecule and has the strongest chemical reactivity. However, the CeSi, PmSi, EuSi, HoSi and TmSi have the bigger gaps than their neighboring diatoms, and the HoSi and TmSi have the largest HOMO-LUMO gaps, exhibiting strongest chemical hardness and dramatically enhanced chemical stabilities for HoSi and TmSi. In addition, the HOMO-LUMO gaps exhibit oscillating behavior from LaSi to LuSi. In other words, the HOMO-LUMO gaps depend on the electrons being fille into $4f$ subshell of rare earth atoms in LnSi.

3.4 *Magnetic moments*

The calculated magnetic moments of LnSi (Ln=La-Lu) are shown in table 2 and figur 3. It can be seen from figur 3 that the total magnetic moment of LnSi (Ln=La-Lu) is increased gradually from LaSi to EuSi, with the electrons in $4f$ subshell of rare earth atom being increased from $4f^0$ in La to $4f^7$ in Eu. Further, magnetic moment decreased from EuSi to LuSi with the electrons in $4f$ subshell of rare earth atom being increased from $4f^7$ in Eu to $4f^{14}$ in Lu. The $4f$ subshell gives rise to strong magnetism because the magnetic effects of the different electrons in the incomplete $4f$ subshell do not cancel each other as they do in a completed subshell. It should be mentioned that the EuSi has the biggest total magnetic moment with Eu atom having $4f^7 6s^2$ electron configuration

4. Conclusions

Density functional method with the hybrid exchange and correlation (mPW3PBE) functional in combination with the 6-31G* basis sets for Si atom and Stuttgart quasi-relativistic effective core potentials (ECP28MWB) for La-Lu elements were carried out. Bond lengths, vibrational frequencies, electron affini ties, and ionization potentials of the neutral and charged LnSi (Ln=La-Lu) diatoms were calculated, and comparisons with available experimental and theoretical values were made, and a good agreement was found. On the basis of the calculated total energies, ground state is assigned for each species. The calculated natural populations of LnSi (Ln=La-Lu) exhibit that the charges are transferred mainly from $6s$ to $5d$, and most of $4f$ subshell in LnSi is inert without involving chemical bonding. The HOMO-LUMO gaps indicate that the HOMO-LUMO gaps are increased and exhibit oscillating behaviors from LaSi to LuSi. The calculated magnetic moments for LnSi (Ln=La-Lu) diatoms exhibit that total magnetic moments depend on the electrons in $4f$ subshell of rare earth atom.

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