

Diffusion Monte Carlo Calculations on Rare-Earths: A Comparative DFT Functionals Study

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Abstract: By employing the DMC method, we investigate the performance of eight DFT exchange-correlation functionals for the ground and excited states of some rare-earths. The functionals to which we investigate are CAM-B3LYP, PBELYP, B3PW91, PBEOP, BMK, M06-2X, M06-L, and M06-HF. The present study shows that M06-2X functional with a large fraction of HF exchange is more preferable than M06 for lanthanides; however, the same is not true for actinides. On the other hand, the full HF exchange functional, M06-HF, is not recommended for both lanthanides and actinides. Furthermore, the calculations find that BMK is the best performers for both the ground and excited states of actinides. Our results also suggest not using functionals containing LYP correlation for systems involving lanthanides.

Keywords: Diffusion Monte Carlo; Density functional theory; Lanthanides; Actinides.

I. INTRODUCTION

Despite the increased interest in the theoretical studies of rare-earths, an accurate calculation for these elements is still missing. In fact, several problems have probably obstructed the correct theoretical description for these systems. One major difficulty is the high number of electronic states arising from open f-shells as well as large relativistic and strong electron-electron correlation effects which should not be neglected in accurate calculations.

Among the most successful methods in treating the strongly correlated electrons systems is the diffusion Monte Carlo (DMC) method which explicitly includes electron-electron correlation effects. Moreover, it scales well with system size, with the computational cost increasing as the cube of the number of electrons.

The most obvious way in which quantum Monte Carlo can be made more efficient is by improving the trial wavefunction. One way to improve the wavefunction is using density functional theory (DFT) for constructing the determinantal part of the wavefunction instead of Hartree-Fock which omits the electron-electron correlation. Although there are a large number of density functionals at different levels of sophistication, conventional hybrid functionals especially the most popular B3LYP functional proved to be a promising tool in many studies [1-3].

Very recently we have tested the performance of the standard B3LYP and M06 functionals for both the ground and the excited states of lanthanides and actinides [4, 5]. Our calculations have indicated that most popular B3LYP functional is not suited for 4f-lanthanides; however, it has given reasonable results for 5f-actinides. On the other hand, the hybrid-meta M06 functional is not accurate enough for both 4f and 5f containing systems.

In this paper, we assess the performance of a variety of DFT functionals including pure (PBELYP, PBEOP), hybrid (B3PW91), range separated hybrid (CAMB3LYP), pure-meta (M06-L), and hybrid-meta (M06, M06-2X, M06-HF, BMK) functionals for calculating the ground and excited states energies for some rare-earths. The ground and excited states energies have been calculated within a DMC framework. The basic form of the wave function that we used is the Slater-Jastrow wave function which is considered the most common and simplest one. The rest of this paper is organized as

follow: In the next section, we briefly describe the DMC method. Then we present and discuss the results. Finally, we give our conclusion.

II. COMPUTATIONAL METHODS

Diffusion Monte Carlo method has been extensively described in the literatures [6-8] so we give here a brief description of it. The diffusion Monte Carlo (DMC) method is a stochastic projector method for solving the imaginary time many-body Schrödinger equation:

$$-\frac{\partial}{\partial \tau} \psi(R, \tau) = \left(-\frac{1}{2} \nabla^2 + V - E_T\right) \psi(R, \tau) \quad (1)$$

where τ is the imaginary time, $\tau = it$ and E_T is the energy offset.

Importance sampling with a trial wavefunction $\psi_T(R)$ is used to improve the statistical accuracy of the simulation and this can be achieved by multiplying Eq. (1) by $\psi_T(R)$ and rearranging

$$-\frac{\partial f(R, \tau)}{\partial \tau} = -\frac{1}{2} \nabla^2 f(R, \tau) + \nabla \cdot [f(R, \tau) \cdot v_D(R)] + [E_L - E_T] f(R, \tau) \quad (2)$$

where $f(R, \tau) = \psi(R, \tau) \psi_T(R)$ interpreted as a probability density and $E_L(R) = \frac{\hat{H} \psi_T(R)}{\psi_T(R)}$ is the local energy.

this equation can be simulated with a random walk having diffusion, a drift, and a branching step and may be written in the integral form:

$$f(R, \tau + \Delta \tau) = \int G(R, R'; \Delta \tau) \cdot f(R, \tau) dR \quad (3)$$

where the Green's function $G(R, R'; \Delta \tau)$ is a solution of the same equation (2) initial and can be interpreted as a probability of transition from a state R to R' . It is possible to use MC method to solve the integral in Eq. (3) but the difficulty is that the precise form of $G(R, R'; \Delta \tau)$ is not known. Fortunately the comparison of the Schrödinger equation with the diffusion equation gives us a clue about how one might approximate the unknown Green's function.

The evolution during the long time interval τ can be generated repeating a large number of short time steps τ . In the limit $\tau \rightarrow 0$, one can make use of the short time approximation for Green's function [9]:

$$G(R, R'; \Delta \tau) \approx (2\pi\Delta\tau)^{-3N/2} \exp\left[-\frac{(R - R' - \Delta\tau \nabla \ln|\psi_T|^2)^2}{2\Delta\tau}\right] \cdot \exp[-\Delta\tau[E_L(R') + E_L(R) - 2E_T]/2] \quad (4)$$

But due to the fermionic nature of electrons, the wavefunction must have positive and negative parts and this is opposite with the assumed nature of ψ which is a probability distribution. So the fixed-node approximation [10] had been used to deal with the fermionic antisymmetry which constrains the nodal surface of ψ to equal that of the antisymmetric trial wavefunction ψ_T .

In this work, we start by generating the wavefunction using the quantum chemistry program Gamess [11]. We make use of CRENBL ECP basis set [12] for all elements except for La atom where CRENBS ECP basis set is being used which proved to be successful for the calculations. DMC technique is used to calculate the ground and the excited states of elements. All QMC computations are performed within Qwalk code [13]. The DMC calculations are performed with a target population of 2000 walkers. In addition a time step of $\tau = 0.001H^{-1}$ is used.

III. RESULTS AND DISCUSSION

We calculate the ground and excited states energies for some lanthanides and actinides using eight different DFT functionals to test the performance of each on this type of systems. The DFT functionals which we investigate involve pure (PBELYP, PBEOP), hybrid (B3PW91), long-range corrected (CAM-B3LYP), pure-meta (M06-L), and hybrid-meta (M06, M06-2X, M06-HF, BMK) functionals. The electronic excitation involves a promotion of an electron with a change of spin from $6s \rightarrow 5d$ and $7s \rightarrow 6d$ for lanthanides and actinides respectively. The results of these tests are shown in tables 1 and 2. We also present our earlier results for B3LYP and M06 for the sake of comparison.

As shown in table 1 that for La, lanthanide element with no 4f-elctrons, there are more than one functional (PBELYP, BPEOP, B3PW91, and BMK) perform comparable or

TABLE 1 Ground state energies G and excited state energies E (due to 6s-5d transition) computed within DMC for lanthanides using different DFT functionals. All energies are in Hartrees.

Method	State	La	Ce	Pr	Nd	Pm	Sm	Eu
B3LYP 28.6630	G	-1.2556	-2.7138	-4.7310	-9.3288	-14.3620	-19.7039	-
	E	-1.2407	-2.5894	-5.3237	-9.3609	-14.0353	-20.2920	-
28.7529 CAMB3LYP 28.7382	G	-1.2575	-2.8421	-4.7196	-9.4035	-14.3319	-20.9882	-
	E	-1.2430	-2.5339	-6.0232	-9.3864	-14.3151	-20.9808	-
28.6129 PBELYP 28.5814	G	-1.2584	-0.7135	-4.3197	-9.4180	-14.4981	-20.4038	-
	E	-1.2378	-0.5912	-4.3955	-9.3901	-14.1224	-19.8811	-
28.7908 B3PW91 28.7349	G	-1.2575	-2.8844	-5.3693	-9.3344	-14.4350	-20.9436	-
	E	-1.2430	-2.5388	-5.2289	-9.3867	-14.4485	-21.0159	-
28.7598 PBEOP 28.5818	G	-1.2546	-2.8274	-5.5047	-9.3296	-14.3674	-20.9213	-
	E	-1.2430	-2.5248	-5.4956	-9.3873	-14.1513	-20.8515	-
28.7877 BMK 28.6261	G	-1.2562	-2.6742	-5.3369	-9.1664	-14.4561	-21.0562	-
	E	-1.2447	-2.6385	-5.2307	-9.1129	-14.1583	-20.9417	-
28.5993 M06 28.6905	G	-1.2149	-2.6600	-5.5325	-8.9997	-14.3154	-20.7858	-
	E	-1.2092	-4.8685	-5.3717	-8.8680	-14.2145	-20.8146	-
28.5964 M06-2X 28.8102	G	-1.2554	-2.6925	-5.9315	-9.4507	-14.3307	-20.8270	-
	E	-1.2407	-2.6564	-5.5199	-9.1683	-14.3955	-20.8286	-
28.7865 M06-L 28.6401	G	-1.1494	-2.6961	-5.2593	-9.2933	-14.6140	-7.1918	-
	E	-1.1705	-2.5024	-5.5317	-9.1109	-13.8596	-8.4506	-
28.8722 M06-HF 28.6857	G	-1.2515	-2.8860	-5.4553	-9.2565	-14.3457	-6.8115	-
	E	-1.2412	-2.7862	-5.4604	-9.1659	-14.3476	-12.5074	-28.8312

Somewhat better than the most popular B3LYP. However, when 4f subshells are being populated, the performance of the conventional B3LYP becomes very poor particularly for the ground state energies as confirmed by the results obtained in our earlier work [4]. Compared the B3LYP ground and excited states energies with the results of hybrid B3PW91, it is clearly turned out that the latter works much better than the former. Note that both functionals contain the same fraction of

exact HF exchange (20%). In fact, a major reason for the poor performance of the most popular B3LYP functional is the use of LYP correlation energy. The results for the ground and excited states of PBELYP and PBEOP functionals notably assure the shortcoming of LYP correlation energy in strongly localized systems.

Regarding to the long-range corrected CAM-B3LYP functional, the calculations indicate that although the inclusion of long-range correction in CAM-B3LYP somewhat improves the results compared to B3LYP, but the results are still unsatisfactory.

We turn now the attention to meta-GGA functionals which we choose to represented them by Minnesota family (M06-2X, M06-L, M06-HF) in addition to BMK. Let us compare them with our earlier results of M06 functional. It is obvious that increasing the percentage of HF exchange from 27% in M06 to 54% HF exchange in M06-2X functional clearly improves the results of ground and excited states as well. This result supports the calculations of Chao-xian Chi et al [15] which indicated that M06-2X is the best performer among all their tested functionals for early lanthanides monoxides. We believe that this improvement is related to the non local HF exchange

TABLE 2 Ground state energies G and excited state energies E (due to 7s-6d transition) computed within DMC for actinides using different DFT functionals. All energies are in Hartrees.

Method	State	Ac	Th	Pa	U	Np	Pu	Am
B3LYP	G	-29.4730	-35.6471	-42.6482	-51.2226	-60.4301	-71.3359	-
74.6117	E	-29.4144	-35.5520	-42.6211	-51.1889	-60.4509	-71.2793	-
74.5618	CAMB3LYP	-29.4760	-35.6088	-42.7265	-51.2420	-60.4752	-71.3514	-
74.8985	E	-29.4355	-35.5936	-42.6493	-51.2042	-60.5129	-71.3482	-
74.9807	PBELYP	-29.4525	-35.6382	-42.6732	-51.2685	-60.4432	-71.4518	-
74.6669	E	-29.4273	-35.5769	-42.6468	-51.1742	-60.3402	-71.3038	-
74.7905	B3PW91	-29.4808	-35.6240	-42.6315	-51.1136	-60.4999	-71.3610	-
74.8358	E	-29.4177	-35.5843	-42.6026	-51.1693	-60.3720	-71.3104	-
74.8220	PBEOP	-29.4593	-35.6418	-42.6663	-51.3063	-60.3587	-71.3585	-
74.7322	E	-29.4183	-35.5468	-42.5659	-51.1406	-60.3779	-71.3201	-
74.7481	BMK	-29.4708	-35.6543	-42.7060	-51.2143	-60.5375	-71.4769	-
74.9876	E	-29.4283	-35.5932	-42.6561	-51.2516	-60.5378	-71.4080	-
74.9129	M06	-29.4749	-35.6118	-42.7546	-51.3074	-53.4227	-54.8674	-
74.3488	E	-29.4575	-35.5724	-42.7316	-51.1787	-55.9839	-56.3098	-
74.3180	M06-2X	-29.4687	-35.5835	-42.6703	-51.1910	-60.3727	-53.7207	-
74.5641	E	-29.4034	-35.5237	-42.5691	-51.2225	-60.4574	-55.4455	-
74.7053	M06-L	-29.4632	-35.6375	-42.6840	-51.2807	-60.4615	-70.9889	-
74.6852	E	-29.4564	-35.5900	-42.6606	-51.2173	-60.3065	-70.6658	-
74.7651	M06-HF	-29.4844	-35.5984	-42.6593	-51.1975	-60.3155	-71.1377	-
74.3808	E	-29.2541	-35.4855	-42.6507	-51.1638	-60.5415	-71.2408	-
74.5007								

Reduces the self-interaction error (SIE) arising from the mean field Coulomb interaction of an electron with itself. In HF theory, there is no SIE because the Hartree-self repulsion energy is exactly cancelled by the Fock-exchange. Hence, SIE in hybrid-DFT is reduced due to the addition of HF-exchange. Meanwhile, M06-HF functional involving 100% non local HF-exchange provides poor results, except for Ce atom, which is a consequence of missing completely static correlation. Unfortunately, M06-L is still can not match the accuracy of hybrid-meta functionals.

For actinides not having 5f-electrons, the picture is similar to La atom. However, in case of 5f-actinides and based on our previous findings [4], B3LYP gives satisfactory results for 5f-actinides unlike 4f-systems. In addition, the improvement achieved by the long-range corrected CAM-B3LYP over B3LYP is small compared to 4f-lanthanides with exception of Am atom due to its similarity with 4f-lanthanides.

It is important also to note that with exception of Am atom, replacing OP by LYP correlation energy does not worsen the results for actinides. In fact, this related to the itinerant character of 5f-electrons in early actinide series. Indeed, one can see from table 2 that B3LYP as well as B3PW91 values for ground and excited states are not much different.

Contrary to 4f-lanthanides, increasing the percentage of HF-exchange in M06-2X functional worsen the results of 5f-actinides compared to M06 except for Am atom. This behavior is likely to originate from the strong static correlation which is more pronounced in actinides than lanthanides. Of course, a large amount of static correlation is lost in this functional due to the replacement of local exchange by a large fraction of non local HF exchange.

On the other hand, the meta-hybrid BMK with 42% HF exchange performs very well for both the ground and excited states of most 5f-actinides. Despite having high percentage of HF exchanges, the results are very encouraging. It appears that the simulated variable exchange in BMK succeeded in achieving an accurate description for the ground and excited states of actinides, confirming that the fraction of HF exchange is not the only factor that determined the qualification of the functional.

IV. CONCLUSION

By using the diffusion Monte Carlo method DMC, we have surveyed a number of different DFT exchange correlation functionals for some rare-earths. At the end of this work one can conclude that: (1) The poor performance of B3LYP functional for lanthanides is traced back to the shortcoming of LYP correlation in strongly localized systems. (2) There is not a large difference between B3LYP and B3PW91 for actinides; however, the latter performs better than the former for lanthanides. (3) M06-2X functional with 54% HF exchange works much better than M06 having 27% HF exchange for lanthanides. However, M06-2X does not improve upon M06 for actinides. (4) M06-HF functional containing 100% HF exchange is not recommended for both 4f and 5f containing systems. (5) The hybrid-meta BMK functional does show the best overall performance for both ground and excited states of most actinides.

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