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Isotope effect of hydrogen and lithium hydride molecules. Application of the dynamic extended molecular orbital method and energy component analysis

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Abstract. In order to explore the isotope effect including the nuclear–electronic coupling and nuclear quantum effects under the one-particle approximation, we apply the dynamic extended molecular orbital (DEMO) method and energy component analysis to the hydrogen and lithium hydride isotope molecules. Since the DEMO method determines both electronic and nuclear wave functions simultaneously by variationally optimizing all parameters embedded in the basis sets, the virial theorem is completely satisfied and guarantees the relation of the kinetic and potential energies. We confirm the isotope effect on internuclear distances, nuclear and electronic wave functions, dipole moment, the polarizability, and each energy component. In the case of isotopic species of the hydrogen molecule, the total energy decreases from the H₂ to the T₂ molecule due to the stabilization of the nuclear–electronic potential component, as well as the nuclear kinetic one. In the case of the lithium hydride molecule, the energy lowering by replacing ⁶Li with ⁷Li is calculated to be greater than that by replacing H with D. This is mainly caused by the small destabilization of electron–electron and nuclear–nuclear repulsion in ⁷LiH compared to ⁶LiH, while the change in the repulsive components from ⁶LiH to ⁶LiD increases.

Key words: Isotope effect – Dynamic extended molecular orbital method – Energy component analysis – Nuclear wave function

1 Introduction

The problem imposed on quantum chemistry is to clarify chemical concepts or chemical phenomena under the quantum mechanical principle. The isotope effect, for example, replacing a hydrogen atom with a deuterium

atom in molecules, is an interesting subject in chemistry, as well as in physics and in other interdisciplinary fields. Many isotope phenomena are observed experimentally, such as, the red shift of the vibrational frequency, the change in the chemical reaction rate [1], the Ubbelohde effect [2], and a drastic change in the phase–transition temperature of hydrogen-bonded ferroelectric materials [3]. Although there are many models and experimental results presented for these phenomena [4], such topics involving the isotope effect continue to remain attractive in both theoretical and experimental fields. Since the chemical nature of hydrogen and deuterium atoms is believed to be the same, the origin of the isotope effect is only related to the difference in their masses; however, it is not yet completely understood how the difference in their masses affects the electronic state and the molecular properties, and what kind of reciprocal action takes place inside the system when a hydrogen nucleus (proton) is replaced with a deuterium nucleus (deuteron). In order to explore these questions, we introduce a first-principle’s molecular orbital (MO) treatment for both electrons and nuclei, which we call the dynamic extended MO (DEMO) method, and analyze their energy components (energy component analysis). This newly developed DEMO method [5, 6] can determine both nuclear and electronic wave functions simultaneously, and expresses the isotope effect including coupling effects between nuclei and electrons directly.

In the conventional MO method only the electronic state is described under the condition of fixed nuclei, i.e., the motion of electrons is evaluated in the field of fixed nuclear charges. It is noted that this electronic Hamiltonian expresses only the electronic state, and no operator terms for the nuclear kinetic energy are taken into account. In order to describe the isotope effect of nuclei, one must solve the nuclear motion on the adiabatic potential under the Born–Oppenheimer approximation [7]. Although the nonadiabatic effects are very small and the adiabatic approach suffices for most chemical systems, the coupling effect between electronic and nuclear

motions and the nonadiabatic effect may be very important in the case of a system containing the hydrogen atom; therefore, the lightest nuclei should be treated as a quantum wave for a better approximation.

The energy component analysis is often used in order to clarify what happens inside the system. Any chemical phenomenon involves a change in the total energy (E), which involves changes in the potential energy (V) and the kinetic energy (T). Analyzing these two energy components in molecules is a useful tool for understanding the nature of chemical phenomena systematically. Pioneering studies on such energy component analysis by Ruedenberg and coworkers [8] provided a very clear interpretation of chemical bond formation. As a matter of fact, a number of papers have been published concerning the origin of Hund's rule [9], the aromaticity [10], the conjugation effect of substituents [11], the nature of the Jahn–Teller effect [12], and the origin of steric hindrance [13] using this analysis. Moreover, the analytical first derivatives of the kinetic and potential energies have been presented [14].

This approach, however, is confronted with a number of difficulties. One of the difficulties is that the values of T and V , which are not eigenvalues but expectation values, depend strongly on the accuracy of the wave function compared with E . Though the conventional basis sets are suitable to improve E , there is no guarantee for the improvement of each energy component. A large number of basis sets involving polarization and diffuse functions are required in order to improve the energy components with the conventional MO calculation [14]. By using the DEMO method, fortunately, two quantum mechanically basic theorems, i.e., the virial theorem and the Hellmann–Feynman theorem, are completely satisfied because of the variational optimization of exponents and centers in the basis set, respectively. The virial theorem guarantees the ratio of the kinetic and potential energy components for all particles involved in any molecular system [15]. It is noted that these theorems are not always satisfied in the conventional MO method.

In order to explore the isotope effect, we have applied both the DEMO method and the energy component analysis to the hydrogen molecule, lithium hydride, and their isotopic species under the Hartree–Fock approximation. We describe the outline of the DEMO method under the Hartree–Fock approximation in the next section. Sects. 3 and 4 show the results of the energy component analysis for hydrogen and lithium hydride isotope molecules, and the energy component dependence of each isotope is discussed. Concluding remarks will be given in Sect. 5.

2 Method

We have proposed the DEMO method [5, 6] in order to obtain both the electronic and nuclear wave functions simultaneously and directly. The total Hamiltonian including M kinds of particles is given by

$$\hat{H}_{\text{tot}} = \sum_I^M \hat{H}_I + \sum_{I>J}^M \hat{V}_{IJ} , \quad (1)$$

where \hat{H}_I and \hat{V}_{IJ} refer to the contribution from the same kind of particles, I , and that from different kinds of particles, I and J , respectively;

$$\hat{H}_I = \sum_{i \in I}^{N_I} \left\{ -\frac{1}{2m_I} \nabla_i^2 + \sum_{i' > i \in I}^{N_I} \frac{Z_I^2}{r_{ii'}} \right\} , \quad (2)$$

$$\hat{V}_{IJ} = \sum_{i \in I}^{N_I} \sum_{j \in J}^{N_J} \frac{Z_I Z_J}{r_{ij}} . \quad (3)$$

In these equations, m_I and Z_I represent the mass and the charge of I th kind particle, and N_I is the number of particles of the I th kind. In the DEMO method, all kinds of particles can be treated as quantum waves. Under the independent-particle (Hartree–Fock) approximation, the total wave function is given by

$$|\Psi\rangle = |\Phi^A\rangle |\Phi^B\rangle \dots |\Phi^M\rangle , \quad (4)$$

where, $|\Phi^I\rangle$ is the antisymmetrized wavefunction for fermion particles of the I th kind. The total energy of this system is given by

$$E_{\text{HF}} = \sum_I^M \left\{ \sum_{i \in I}^{\text{IMO}} n_i^I h_{ii}^I + Z_I^2 \sum_{i, i' \in I}^{\text{IMO}} [\alpha_{ii'}^I (\phi_i \phi_i | \phi_{i'} \phi_{i'}) + \beta_{ii'}^I (\phi_i \phi_{i'} | \phi_i \phi_{i'})] \right\} + \sum_{I>J}^M Z_I Z_J \sum_{i \in I}^{\text{IMO}} \sum_{j \in J}^{\text{JMO}} n_i^I n_j^J (\phi_i \phi_i | \phi_j \phi_j) , \quad (5)$$

where ϕ_i and ϕ_j are the MOs of the I th and J th kinds of particles, h_{ii}^I is a one-particle integral, $(\phi_i \phi_i | \phi_{i'} \phi_{i'})$ and $(\phi_i \phi_{i'} | \phi_i \phi_{i'})$ are Coulomb and exchange integrals between the same kinds of particles, and $(\phi_i \phi_i | \phi_j \phi_j)$ is the Coulomb integral between different kinds of particles. Furthermore, the coefficients n_i^I are the occupation numbers of ϕ_i , α and β are Coulomb and exchange coupling constants, IMO is the number of MOs in the I th kind of particle. The position of the I th kind of particle is evaluated as the expectation value of the coordinates,

$$R = \langle \Phi^I | \hat{R} | \Phi^I \rangle . \quad (6)$$

The internuclear distance obtained by the DEMO method corresponds to the expectation value (average internuclear distance), which is longer than the equilibrium internuclear distance defined by the conventional MO method because of the anharmonic nature of the potential.

The electronic and nuclear MOs are expressed as a linear combination of primitive Cartesian Gaussian-type functions (GTFs),

$$\phi_i = \sum_r^{\text{IAO}} C_{ri}^I \chi_r^I ,$$

$$\chi_r(l_r, m_r, n_r, \alpha_r) = (x - X_r)^{l_r} (y - Y_r)^{m_r} (z - Z_r)^{n_r} \times \exp \left[-\alpha_r \{ (x - X_r)^2 + (y - Y_r)^2 + (z - Z_r)^2 \} \right] , \quad (7)$$

where C_{ri}^I , $\{X_r, Y_r, Z_r\}$, and α_r are the linear combination of GTF (LCGTF) coefficients, the coordinates of the GTF center, and the GTF exponent, respectively. IAO is the number of GTFs in the I th kind of particle. In the conventional LCGTF-MO calculation, only LCGTF coefficients are determined with the variational theorem by fixing the other parameters; however, the exponents for nuclear GTFs have not yet been determined by optimization. To our knowledge, no report exists for the analytical optimization of both GTF exponents and centers for many-electron molecular systems, though the optimization for one-electron systems [16], the optimization of only GTF exponents [17], and the optimization of only GTF centers [18] have been reported. In our approach, we adopt the fully variational treatment for molecular orbitals [19], where all parameters, LCGTF coefficients, GTF exponents, and their centers (denoted as Ω) are optimized for both electronic and nuclear GTFs. Since the GTF exponents and centers are mutually dependent, nonlinear optimization must be carried out. We have used the analytical gradient

$$\begin{aligned} \frac{\partial}{\partial \Omega_X^I} E_{\text{HF}} = & \sum_{i \in I} n_i^I \sum_{rs} C_{ri}^I C_{si}^I \frac{\partial h_{rs}^I}{\partial \Omega_X^I} \\ & + Z_I^2 \sum_{i, i' \in I} \sum_{rstu} \left\{ (\alpha_{ii'}^I C_{ri}^I C_{si}^I C_{ti}^I C_{ui'}^I \right. \\ & \left. + \beta_{ii'}^I C_{ri}^I C_{si'}^I C_{ti}^I C_{ui'}^I) \frac{\partial (rs|tu)}{\partial \Omega_X^I} \right\} \\ & + Z_I \sum_{i \in I} n_i^I \sum_{rs \in I} \sum_{l \neq J} Z_J \sum_{j \in J} n_j^J \\ & \times \sum_{tu \in J} C_{ri}^I C_{st}^I C_{tj}^J C_{uj}^J \frac{\partial (rs|tu)}{\partial \Omega_X^I} \\ & - \sum_{i \in I} n_i^I \epsilon_i^I \sum_{rs \in I} C_{ri}^I C_{si}^I \frac{\partial S_{rs}^I}{\partial \Omega_X^I}, \quad (8) \end{aligned}$$

where ϵ_i^I is the orbital energy, $\partial h_{rs}^I / \partial \Omega_X^I$, $\partial (rs|tu) / \partial \Omega_X^I$, and $\partial S_{rs}^I / \partial \Omega_X^I$ are the derivatives of one-, two-particle, and overlap integrals, respectively. The updated Hessian matrix is constructed from the cumulative gradients by using the Davidon, Fletcher, and Powell method [20]. The convergence of optimization is judged when the maximum value and the root mean square of gradients become less than 1×10^{-7} and 5×10^{-8} , respectively. In this calculation, all GTF centers are placed and optimized along the x -axis, so that both molecular translational and rotational energies are excluded from the nuclear kinetic energy.

3 Results and discussion of hydrogen molecules

We have applied the DEMO method within the Hartree-Fock approximation to the hydrogen molecular systems by including the coupling effect between nuclei and electrons. While hydrogen nuclei are treated as +1 point charges in the conventional MO calculation, we have

employed GTFs for a proton basis set in addition to the electron basis set in the DEMO method. The differences for proton, deuteron, and triton appears as the masses in the kinetic energy operators, whose values are 1836.59, 3669.48, and 5496.92 a.u., respectively [21]. Since the exchange effect among the same kind of nucleus is very small, the nuclear exchange terms in Eq. (5) are not taken into account in the present calculation. This approximation corresponds to different spins for the same kind of nucleus, i.e. the p -hydrogen molecule. All GTFs are placed along the x -axis, with the origin at $R/2$.

3.1 Basis-set dependence of H_2

The schematic description of the electronic and nuclear densities with each GTF basis set optimized for H_2 , HD , and D_2 molecules is illustrated in Fig. 1. The three s and a single s GTFs are employed for the electronic and nuclear basis sets (hereafter denoted as $[3s:1s]$), and all GTF exponents and centers are optimized simultaneously. Since the nuclear kinetic effect is directly taken into account by this method, the H/D isotope effect is clearly demonstrated in the internuclear distances (R), polarizabilities (α_{xx}), as well as in the exponent values of a proton and a deuteron. The exponent of a deuteron (about 33) is greater than that of a proton (about 22), i.e. the nuclear wave function of a deuteron is more localized than that of a proton. It is interesting that the relaxation of the electronic state is clearly observed by deuteration, i.e., the electronic density on D is also more localized than that on H. Therefore, the HD molecule has a nonvanishing value of the dipole moment (μ_x), while H_2 and D_2 molecules do not. In order to choose a suitable basis-set for further discussion, we show the basis-set dependence for the H_2 molecule with the DEMO method.

In order to observe the basis-set dependence in the DEMO method, we show the results of variationally optimized GTFs with a number of basis sets for H_2 in Table 1. We have applied 3s, 4s, and 5s GTFs for the electronic basis set, and 1s, 2s, 1s 1p, and 1s 1p 1d GTFs for the protonic basis set. We have not used the polarization (p -type) function for the electronic basis set because the electronic polarization effect is already taken into account by optimizing the GTF centers [19]. In order to check the role of the polarization functions for the nuclear basis set, we have employed the calculation with these protonic basis sets. Table 1 also shows the total energy, E_{HF} , relative energy, ΔE , virial ratio, and average nuclear positions. It is noted that the virial ratio is always very close to 2, irrespective of the number of basis set [15].

Since we have no restriction for the optimization of both electronic and nuclear GTF centers, we obtain the different GTF centers for the electron and the nucleus. All the centers of the electronic GTFs are calculated to be inside the average nuclear positions, which means that the electrons are gathered in the bonding region. In the conventional MO method, such an electronic polarization effect is expressed only with the LCGTF coefficients under the condition of fixed GTF exponents and centers.

Fig. 1. A schematic illustration of electronic and nuclear densities, internuclear distances R , dipole moments μ_x , and polarizabilities α_{xx} , with variationally optimized $[3s:1s]$ basis sets for hydrogen molecules. The values of α denote the Gaussian-type function (GTF) exponents for the nucleus

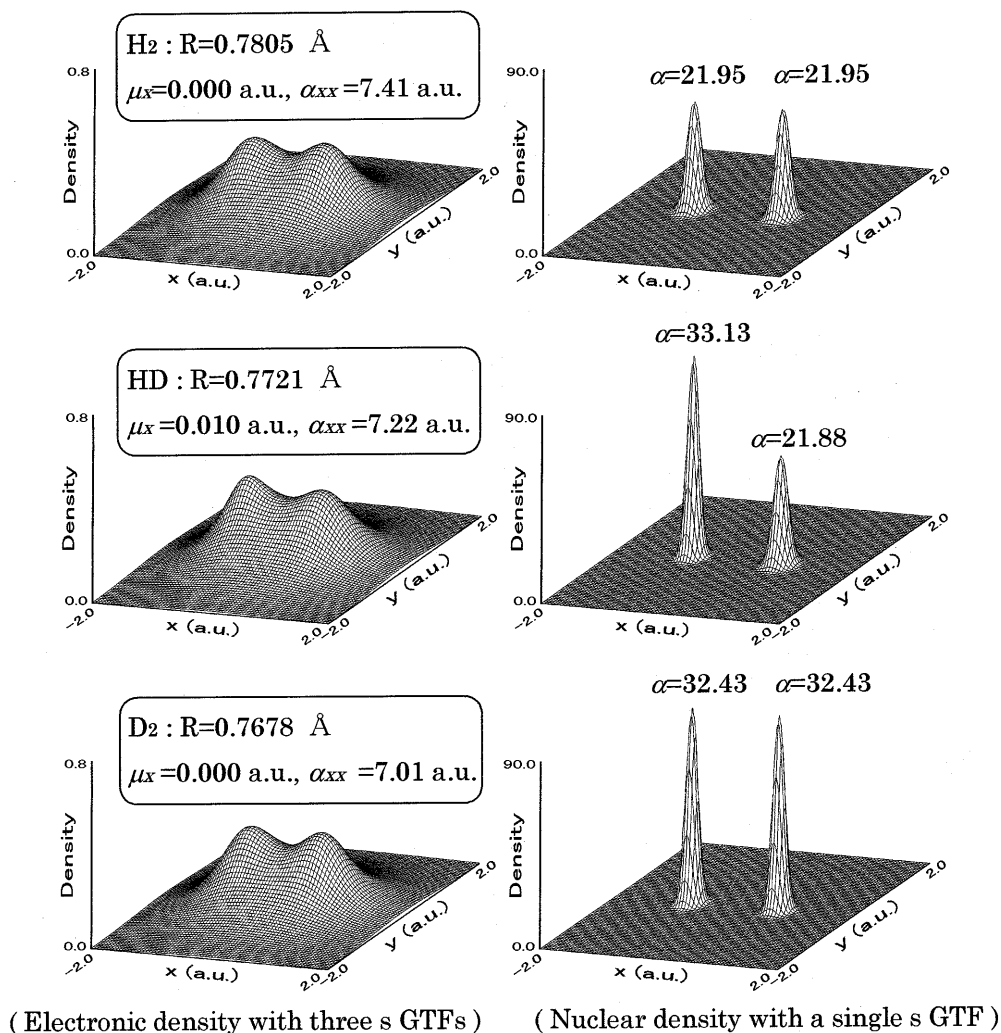


Table 1 shows that the internuclear distance calculated from the expectation value of the nuclear position becomes a little shorter as the number of basis sets increases in the DEMO method. For instance, the average internuclear distances calculated with the $[3s:1s]$, $[4s:1s]$, and $[5s:1s]$ basis sets are 0.7803, 0.7787, and 0.7786 Å, respectively. This is due to the increase in the electronic and nuclear densities in the bonding region. Accordingly the protonic GTF exponent becomes greater as the number of electronic basis sets increases, i.e., 21.95, 22.35, and 22.43 for the $[3s:1s]$, $[4s:1s]$, and $[5s:1s]$ basis sets.

In the $[4s:1s]$ basis set, the center of a single protonic s -type GTF is calculated to be at ± 0.3894 Å, which is located outside all electronic GTF centers. This means that the anharmonic effect is described even though we used only a single s -type GTF for the nucleus. In the case of the $[4s:2s]$ basis set, the average internuclear distance is 0.7787 Å, which is almost identical to that with the $[4s:1s1p]$ basis set. In the case of the $[4s:1s1p]$ basis set, the protonic $1s$ and $1p$ GTFs have different center positions at 0.3106 and 0.3428 Å, the MO coefficients of which are 0.9530 and 0.6484, respectively. The average internuclear distance with the $[4s:1s1p]$ basis set gives 0.7760 Å, i.e., the proton density increases in the outer

region of the two protonic GTF centers. The p -type GTF is used to express the anharmonic effect more flexibly. The average internuclear distance with the $[4s:1s1p1d]$ basis set gives 0.7759 Å, which is almost identical to that with $[4s:1s1p]$.

The total energy decreases as the number of basis functions increases, in accord with the fact that the expanded variational space improves the wave function. The improvement in the total energy from $3s$ to $4s$ electronic GTFs is 1.40 kcal/mol, and that from $3s$ to $5s$ is 1.56 kcal/mol. The improvement in the total energy from $1s$ to $1s$ $1p$ nuclear GTFs is about 0.22 kcal/mol, which is much larger than that from $1s$ to $2s$ or from $1s$ $1p$ to $1s$ $1p$ $1d$ GTFs (both about 0.01 kcal/mol). Consequently, $1s$ $1p$ GTFs are required for the nuclear basis set, and we have adopted the $[4s:1s1p]$ basis set for further discussion of hydrogen isotope molecules.

3.2 Hydrogen isotope molecules with the $[4s:1s1p]$ basis set

In order to discuss the isotope effect on the electronic and nuclear wave functions more clearly, we have employed the DEMO calculation with the $[4s:1s1p]$

Table 1. Variationally optimized Gaussian-type functions (GTF) basis sets for the H₂ molecule using the dynamic extended molecular orbital (DEMO) method

	[3s:1s]	[3s:2s]	[3s:1s p]	[3s:1s p d]	[4s:1s]	[4s:2s]	[4s:1s p]	[4s:1s p d]	[5s:1s]	[5s:2s]	[5s:1s p]	[5s:1s p d]
E_{HF} (hartree)	-1.049768	-1.049778	-1.050172	-1.050184	-1.052003	-1.052015	-1.052371	-1.052385	-1.052254	-1.052267	-1.052626	-1.052641
ΔE (kcal/mol)	0.00	0.01	0.25	0.26	1.40	1.41	1.63	1.64	1.56	1.57	1.79	1.80
$(V/T) + 2$	3.00E-10	7.28E-07	5.95E-08	1.40E-09	-7.90E-09	4.53E-07	3.50E-09	7.00E-09	1.03E-06	-2.55E-08	8.84E-08	2.13E-07
Electron Center ^a												
<i>s</i>	0.3729	0.3729	0.3713	0.3712	0.3823	0.3823	0.3809	0.3808	0.3871	0.3870	0.3853	0.3852
<i>s</i>	0.3403	0.3403	0.3387	0.3387	0.3479	0.3479	0.3472	0.3472	0.3653	0.3655	0.3641	0.3641
<i>s</i>	0.3175	0.3175	0.3148	0.3147	0.3348	0.3348	0.3326	0.3326	0.3396	0.3395	0.3381	0.3381
<i>s</i>					0.3027	0.3027	0.3023	0.3023	0.3311	0.3312	0.3286	0.3286
<i>s</i>									0.2928	0.2926	0.2924	0.2923
Exponent												
<i>s</i>	3.8447	3.8469	3.8083	3.8084	7.2737	7.2865	7.2591	7.2715	11.7162	11.7925	11.5843	11.6297
<i>s</i>	0.7017	0.7019	0.6969	0.6968	1.5182	1.5196	1.5220	1.5237	2.9612	2.9772	2.9106	2.9170
<i>s</i>	0.1633	0.1634	0.1628	0.1628	0.4073	0.4076	0.4086	0.4089	0.9095	0.9131	0.8926	0.8937
<i>s</i>					0.1224	0.1224	0.1227	0.1228	0.2944	0.2952	0.2909	0.2911
<i>s</i>									0.1015	0.1017	0.1009	0.1010
Nucleus Center ^a												
<i>s</i>	0.3902	0.3879	0.3088	0.3180	0.3894	0.3869	0.3106	0.3195	0.3893	0.3866	0.3107	0.3193
<i>s</i>		0.3928				0.3919				0.3916		
<i>p</i>			0.3420	0.3473			0.3428	0.3478			0.3428	0.3477
<i>d</i>				0.3850				0.3843				0.3845
Exponent												
<i>s</i>	21.9474	25.2739	20.2213	19.5888	22.3471	26.3292	20.6763	19.8723	22.4269	26.9129	20.7378	19.9051
<i>s</i>		19.0205				19.4129				19.6314		
<i>p</i>			20.4508	19.6022			20.9012	19.8850			20.9772	19.9191
<i>d</i>				25.2420				25.6495				25.8470
R^b (Å)	0.7803	0.7803	0.7773	0.7772	0.7787	0.7787	0.7760	0.7759	0.7786	0.7787	0.7759	0.7758

^a Only the positive *x*-coordinates (Å) of GTF centers are shown^b Expectation value of the internuclear distance

basis set to various hydrogen isotope molecules, i.e., H₂, HD, D₂, HT, DT, and T₂. The variationally optimized GTF centers, exponents, and the linear combination of atomic orbitals coefficients for these molecules are given in Table 2. The Hartree–Fock energy, the relative energy ΔE , the virial ratio, the dipole moment, the internuclear distance R , and the energy components T and V are summarized in Table 3. We have divided the total kinetic energy (T) into the nuclear (T_n) and electronic (T_e) kinetic energies, and the total potential energy (V) is also divided into the nuclear–electronic (V_{ne}), electronic–electronic (V_{ee}), and nuclear–nuclear (V_{nn}) potential parts. These relative energy components are also shown in Table 3.

The virial ratios are calculated to be very close to 2 within an accuracy of 10^{-7} for all cases, which confirms the reliability of the energy components, T and V , and so we can discuss the isotope effect using these values. The Hartree–Fock energy with the conventional MO method is -1.13217 hartree, which gains 99.9% of the total energy of the Hartree–Fock limitation of -1.1336 hartree

[22]. The energy determined with the conventional MO method (-1.13217 hartree) is lower than that with the DEMO method, because the nuclear kinetic energies are not included in the conventional MO method. It is clearly shown that the Hartree–Fock energy calculated with the DEMO method decreases as the nuclear mass increases. The energy change from H₂ to T₂ is calculated to be -19.92 kcal/mol. The origin of such an energy change owing to the isotope effect is discussed in the following subsections using the data in Tables 2 and 3 by applying the energy component analysis.

3.2.1 Optimized basis sets

As shown in Table 2, all optimized electronic GTF exponents for the DEMO method have smaller values than those of the conventional MO treatment indicated in the first column. Since the nuclei are treated as a quantum wave in the DEMO method, the electronic wave function becomes more diffuse compared to the conventional electronic wave function.

Table 2. Variationally optimized $[4s:1s1p]$ GTFs for various isotopes of a hydrogen molecule using the DEMO method

	Point charge	DEMO method					
	H ₂	H ₂	HD	D ₂	HT	DT	T ₂
Electronic GTFs		H	H	D	H	D	T
Center (Å)							
<i>s</i>	0.3649	0.3809	0.3774	0.3760	0.3761	0.3746	0.3738
<i>s</i>	0.3364	0.3472	0.3466	0.3435	0.3451	0.3452	0.3420
<i>s</i>	0.3196	0.3326	0.3225	0.3286	0.3205	0.3197	0.3268
<i>s</i>	0.2903	0.3023	0.0389	0.2987	0.0353	0.0398	0.2972
		H	D	D	T	T	T
<i>s</i>	-0.3649	-0.3809	-0.3811	-0.3760	-0.3801	-0.3771	-0.3738
<i>s</i>	-0.3364	-0.3472	-0.3692	-0.3435	-0.3694	-0.3660	-0.3420
<i>s</i>	-0.3196	-0.3326	-0.3266	-0.3286	-0.3268	-0.3230	-0.3268
<i>s</i>	-0.2903	-0.3023	-0.3660	-0.2987	-0.3643	-0.3625	-0.2972
Exponent		H	H	D	H	D	T
<i>s</i>	16.3515 (0.0125)	7.2591 (0.0198)	7.0104 (0.0209)	8.5068 (0.0183)	7.0438 (0.0208)	8.1476 (0.0196)	9.2397 (0.0175)
<i>s</i>	2.4516 (0.0876)	1.5220 (0.1147)	1.4328 (0.1241)	1.6799 (0.1093)	1.4407 (0.1236)	1.5641 (0.1195)	1.7675 (0.1064)
<i>s</i>	0.5599 (0.2702)	0.4086 (0.2761)	0.3719 (0.3023)	0.4375 (0.2754)	0.3744 (0.3016)	0.3943 (0.3030)	0.4529 (0.2750)
<i>s</i>	0.1494 (0.2430)	0.1227 (0.1989)	0.1078 (0.3132)	0.1284 (0.2076)	0.1086 (0.3161)	0.1118 (0.3274)	0.1313 (0.2122)
		H	H	D	T	T	T
<i>s</i>	16.3515 (0.0125)	7.2591 (0.0198)	14.3637 (0.0075)	8.5068 (0.0183)	16.0430 (0.0071)	16.4410 (0.0068)	9.2397 (0.0175)
<i>s</i>	2.4516 (0.0876)	1.5220 (0.1147)	3.3554 (0.0441)	1.6799 (0.1093)	3.5907 (0.0425)	3.6952 (0.0412)	1.7675 (0.1064)
<i>s</i>	0.5599 (0.2702)	0.4086 (0.2761)	0.9717 (0.1539)	0.4375 (0.2754)	1.0100 (0.1526)	1.0386 (0.1493)	0.4529 (0.2750)
<i>s</i>	0.1494 (0.2430)	0.1227 (0.1989)	0.3103 (0.2527)	0.1284 (0.2076)	0.3174 (0.2549)	0.3263 (0.2533)	0.1313 (0.2122)
Nuclear GTFs		H	H	D	H	D	T
Center (Å)							
<i>s</i>		0.3106	0.3070	0.3192	0.3054	0.3175	0.3236
<i>p</i>		0.3428	0.3394	0.3454	0.3379	0.3438	0.3469
Exponent							
<i>s</i>		20.6763 (0.9530)	20.6709 (0.9520)	30.8404 (0.9557)	20.6882 (0.9518)	30.8113 (0.9551)	38.7321 (0.9570)
<i>p</i>		20.9012 (0.6484)	20.9126 (0.6532)	31.1093 (0.6413)	20.9337 (0.6542)	31.0951 (0.6436)	39.0342 (0.6374)
Nucleus		H	D	D	T	T	T
Center (Å)							
<i>s</i>		-0.3106	-0.4090	-0.3192	-0.3288	-0.3255	-0.3236
<i>p</i>		-0.3428	-0.4100	-0.3454	-0.3517	-0.3485	-0.3469
Exponent							
<i>s</i>		20.6763 (0.9530)	31.1105 (0.9615)	30.8404 (0.9557)	38.9393 (0.9582)	38.9964 (0.9576)	38.7321 (0.9570)
<i>p</i>		20.9012 (0.6484)	34.8151 (0.2651)	31.1093 (0.6413)	39.2383 (0.6291)	39.3079 (0.6328)	39.0342 (0.6374)

Linear combination of GTF coefficients are shown in parentheses

Table 3. Energy components analysis for a hydrogen molecule and its isotopes using the $[4s:1s1p]$ basis set with the DEMO method

	Point charge	DEMO method					
	H ₂	H ₂	HD	D ₂	HT	DT	T ₂
E_{HF} (hartree)	-1.132175	-1.052371	-1.063356	-1.074137	-1.068382	-1.079279	-1.084123
ΔE (kcal/mol)		0.00	-6.89	-13.66	-10.85	-16.88	-19.92
$(V/T) + 2$	-3.50E-08	3.50E-09	-3.00E-10	-4.95E-08	-4.30E-09	1.34E-08	2.87E-08
Dipole (a.u.)	0.0000	0.0000	0.0099	0.0000	0.0144	0.0041	0.0000
R (Å)	0.7339	0.7760	0.7699	0.7638	0.7671	0.7610	0.7584
Exptl. R_c (Å) ^a	0.7414						
Exptl. R (Å) ^a		0.7511	0.7498	0.7484	0.7493	0.7476	0.7469
T (hartree)	1.132175	1.052371	1.063356	1.074137	1.068382	1.079279	1.084123
ΔT (kcal/mol)		0.00	6.89	13.66	10.05	16.88	19.92
T_c (hartree)	1.132175	1.016078	1.031640	1.047167	1.038866	1.054445	1.061558
ΔT_c (kcal/mol)		0.00	9.77	19.51	14.30	24.08	28.54
T_n (hartree)		0.018147 (H)	0.01874 (H)	0.013485 (D)	0.018197 (H)	0.013486 (D)	0.011282 (T)
ΔT_n (kcal/mol)		0.00	0.02	-2.93	0.03	-2.92	-4.31
T_n (hartree)		0.018147 (H)	0.013542 (D)	0.013485 (D)	0.011320 (T)	0.011348 (T)	0.011282 (T)
ΔT_n (kcal/mol)		0.00	-2.89	-2.93	-4.28	-4.27	-4.31
V (hartree)	-2.264349	-2.104742	-2.126712	-2.148274	-2.136764	-2.158558	-2.168246
ΔV (kcal/mol)		0.00	-13.79	-27.32	-20.09	-33.77	-39.85
V_{ne} (hartree)	-3.646716	-3.417512	-3.449165	-3.480520	-3.463680	-3.495293	-3.509316
ΔV_{ne} (kcal/mol)		0.00	-19.86	-39.54	-28.97	-48.81	-57.61
V_{ee} (hartree)	0.661348	0.632206	0.686230	0.640370	0.638096	0.642182	0.644064
ΔV_{ee} (kcal/mol)		0.00	2.52	5.12	3.70	6.26	7.44
V_{nn} (hartree)	0.721019	0.680564	0.686224	0.691876	0.688821	0.694553	0.697006
ΔV_{nn} (kcal/mol)		0.00	3.55	7.10	5.18	8.78	10.32

^a Ref. [23]

The homonuclear molecules have the same exponent values for the nuclear ($1s, 1p$) GTFs, which are calculated to be (20.7, 20.9), (30.8, 31.1), and (38.7, 39.0) for H₂, D₂, and T₂, respectively. The optimized electronic GTF exponents and centers are also obtained symmetrically for these molecules. As the nuclear mass increases from H₂ to T₂, the electronic GTF exponents become large, as do the nuclear ones.

On the other hand, the heteronuclear molecules, HD, HT, and DT, have different exponents and their GTF centers result in nonsymmetry. When considering the LCGTF coefficients in Table 2, the most diffuse electronic GTF (fourth s) is dominant in describing the electronic MO. It is interesting that the position of this diffuse GTF moves from the light nucleus to the heavy one in the case of heteronuclear molecules, and their centers locate very close to the middle of the bond: 0.0389, 0.0353, and 0.0398 Å in HD, HT, and DT, respectively. This means that such a diffuse GTF plays the role of the polarization function as well and gives the polarized ionic structure of H^{δ+}D^{δ-}, H^{δ+}T^{δ-}, and D^{δ+}T^{δ-}. As a result, these molecules have the dipole moment values shown in Table 3. The calculated dipole moment of HD is 0.0099 a.u., which is, however, greater than the experimental value of 0.00023 a.u. [23].

3.2.2 Internuclear distance

As seen in Table 3, the equilibrium internuclear distance of H₂ is calculated to be 0.7339 Å with the conventional MO method, which is the bottom of the well in the

potential-energy curve. This internuclear distance is shorter than the experimental equilibrium one of 0.7414 Å [23] because of the lack of electron correlation in the scheme of the Hartree–Fock method.

Noting that the internuclear distance, R , obtained by the DEMO method corresponds to the expectation value of the quantum nucleus (average internuclear distance), we observe a clear difference in the internuclear distances among these hydrogen molecules with the DEMO method. The calculated average internuclear distances from the DEMO method are 0.7760, 0.7699, 0.7638, 0.7671, 0.7610, and 0.7584 Å for H₂, HD, D₂, HT, DT, and T₂, respectively. A comparison of the internuclear distances between the DEMO and conventional MO treatments indicates the following relationship,

$$R(\text{Conventional MO}) < R_{\text{T}_2} < R_{\text{D}_2} < R_{\text{H}_2} . \quad (9)$$

Considering the anharmonic nature of the potential, the average internuclear distance becomes larger as the energy of the zero-point vibrational level increases. In fact, the experimental average internuclear distances are 0.7511, 0.7498, 0.7484, 0.7493, 0.7476, and 0.7469 Å for H₂, HD, D₂, HT, DT, and T₂, respectively. This trend agrees with the result shown in Eq. (9). Since the nuclear kinetic effect is directly taken into account in the DEMO method, we can clearly demonstrate the H/D/T isotope effect in the internuclear distance of a hydrogen molecule. Although the calculated internuclear distances are longer than the experimental one, we would expect an improvement using many-body corrections, which are not treated in the present DEMO calculation.

3.2.3 Kinetic energy

The total kinetic energy, T , becomes larger as the nuclear mass increases. As shown in Table 3, the kinetic energy change is +19.92 kcal/mol from H_2 to T_2 . In order to discuss the origin of this energy change, we divide the total kinetic energy into two components, T_n and T_e .

The nuclear kinetic energy, T_n , decreases as the nuclear mass increases, i.e., ΔT_n is -8.62 kcal/mol from H_2 to T_2 . This is caused by the increment of the nuclear mass, which affects the localization of the nuclear wave as seen in the large exponent value of the nuclear GTF for T_2 . Since all parameters are optimized in the present DEMO calculation, both the translational and rotational energies are excluded, and only the vibrational energy is included in the nuclear kinetic energy; however, the nuclear kinetic energy of H_2 is calculated to be 0.0362 hartree = 7940 cm^{-1} , which is much greater than the experimental zero-point energy (2170 cm^{-1}) due to the lack of many-body effects such as electronic correlation and electronic-nuclear correlation.

On the other hand, the electronic kinetic energy, T_e , becomes larger as the nuclear mass increases. The change in the electronic kinetic energy, ΔT_e , is 28.54 kcal/mol from H_2 to T_2 . Seeing the optimized electronic GTF centers and exponents in Table 2, the GTF centers move slightly toward the inside and their exponents become greater as the nuclear mass increases. As shown in Sect. 3.2.2, the internuclear distance of the hydrogen molecule becomes shorter as the nuclear mass increases. This change in the internuclear distance causes the deformation of the electron distribution, and so the electron density between the hydrogen nuclei increases. The region of electron movement becomes restricted due to the shortening of the internuclear distance and the increase in the electron density. Accordingly the increase in T_e turns out to be much larger than the decrease in T_n as the nuclear mass increases.

3.2.4 Potential energy

The total potential energy, V , decreases as the nuclear mass increases as shown in Table 3. ΔV is -39.85 kcal/mol from H_2 to T_2 . Of course this value is exactly twice $-\Delta T$ in this calculation. The large energy lowering of the nuclear-electronic potential energy, $\Delta V_{ne} = -57.61$ kcal/mol, is observed when changing from H_2 to T_2 . This is caused by the increase in the overlap between the nuclear and electronic wave functions for a T_2 molecule, because the internuclear distance of T_2 is shorter than that of H_2 . Note that ΔV_{ne} between H_2 and T_2 of -57.61 kcal/mol is about 7 times larger than ΔT_n of -8.32 kcal/mol. Consequently, ΔV_{ne} is the dominant factor for the total energy change, ΔE , in the DEMO calculation within the Hartree–Fock approximation.

We also show the repulsive components between electrons (V_{ee}) and between nuclei (V_{nn}) in Table 3. These repulsive components with the DEMO method are smaller than those with the conventional MO method. Since the nucleus is described by wave functions which have a certain distribution in the present method, the electronic wave function becomes more diffuse than that with the conventional MO method, and gives less

repulsive electronic energy. Since the internuclear distance with the DEMO method is longer than that with the conventional MO method, the nuclear repulsion energy obtained with the DEMO method is smaller than that obtained with the conventional MO method. The stabilization of V arises from the large attractive contribution of V_{ne} compared with $V_{ee} + V_{nn}$ in the region of chemical bonding. The change in repulsion among electrons (ΔV_{ee}) and that between nuclei (ΔV_{nn}) are calculated to be 7.44 and 10.32 kcal/mol from H_2 to T_2 , respectively, due to the shorter internuclear distance for T_2 .

Consequently we have clearly confirmed the H/D/T isotope effect on internuclear distance, nuclear and electronic wave functions, and each energy component for the DEMO method within the Hartree–Fock approximation. We found that the dominant factor for the total energy stabilization from H_2 to T_2 is caused by the difference in the electronic–nuclear potential components, and the secondary factor is due to the difference in the nuclear kinetic energy. The changes in the electronic kinetic, electronic–electronic potential, and nuclear–nuclear potential components behave in the opposite direction to the change in the total energies.

4 Results and discussion of lithium hydride molecules

We have also applied the DEMO method to the various isotopes of lithium hydride. We have optimized the GTFs of the nuclear basis set for the hydrogen and lithium nuclei, as well as the GTFs of the electronic basis set in the DEMO method, while lithium and hydrogen nuclei are treated as +3 and +1 point charges in the conventional MO calculation. We have employed electronic $4s$ GTFs and nuclear $1s$ $1p$ GTFs for both the lithium and the hydrogen atoms. We have taken the masses of the ${}^6\text{Li}$ and ${}^7\text{Li}$ nuclei to be 10958.90 and 12782.45 a.u., respectively [21]. All GTFs are placed along the x -axis, and all parameters are optimized. We have set the origin to the $1s$ nuclear GTF center for the lithium atom after optimization.

4.1 Optimized basis sets

The variationally optimized GTF centers and exponents for ${}^6\text{LiH}$, ${}^6\text{LiD}$, ${}^6\text{LiT}$, ${}^7\text{LiH}$, ${}^7\text{LiD}$, and ${}^7\text{LiT}$ are shown in Table 4. We have adopted the electronic $4s$ GTFs for both the lithium and the hydrogen atoms as the initial electronic GTF condition. After the fully variational optimization, the centers of the first five electronic GTFs are almost 0.00 Å, which is the position of the lithium nuclear $1s$ GTF, while the sixth electronic GTF is located at the hydrogen nucleus. The last two electronic GTFs become diffuse and move a little toward the lithium nucleus. As a result, the minimum energy is obtained with $5s$ electronic GTFs for lithium and $3s$ ones for hydrogen atoms, rather than $4s$ electronic GTFs for each atom. This fact is confirmed by using the various kinds of initial conditions of the GTF centers and exponents. The result demonstrates that the balance of

Table 4. Variationally optimized $[4s:1s1p]$ GTFs for various isotopes for a lithium hydride molecule using the DEMO method

	Point charge	DEMO method					
	LiH	${}^6\text{LiH}$	${}^6\text{LiD}$	${}^6\text{LiT}$	${}^7\text{LiH}$	${}^7\text{LiD}$	${}^7\text{LiT}$
Electronic GTFs		${}^6\text{Li}$	${}^6\text{Li}$	${}^6\text{Li}$	${}^7\text{Li}$	${}^7\text{Li}$	${}^7\text{Li}$
Center (Å)							
<i>s</i>	-0.084	-0.097	-0.097	-0.097	-0.096	-0.096	-0.096
<i>s</i>	0.000	0.000	0.000	0.000	0.000	0.000	0.000
<i>s</i>	0.000	0.000	0.000	0.000	0.000	0.000	0.000
<i>s</i>	0.000	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001
<i>s</i>	-0.014	-0.015	-0.015	-0.016	-0.015	-0.015	-0.015
		H	D	T	H	D	T
<i>s</i>	1.625	1.654	1.646	1.642	1.653	1.645	1.642
<i>s</i>	1.509	1.493	1.496	1.497	1.493	1.496	1.497
<i>s</i>	1.280	1.279	1.280	1.280	1.278	1.279	1.280
Exponent		${}^6\text{Li}$	${}^6\text{Li}$	${}^6\text{Li}$	${}^7\text{Li}$	${}^7\text{Li}$	${}^7\text{Li}$
<i>s</i>	222.061	187.999	188.083	188.018	190.651	188.662	190.206
<i>s</i>	27.652	71.277	71.264	71.256	72.655	72.642	72.634
<i>s</i>	14.663	12.246	12.243	12.241	12.385	12.382	12.381
<i>s</i>	3.216	2.866	2.865	2.865	2.887	2.886	2.886
<i>s</i>	0.8154	0.7601	0.7600	0.7600	0.7636	0.7635	0.7635
		H	D	T	H	D	T
<i>s</i>	2.564	1.865	2.011	2.086	1.866	2.011	2.086
<i>s</i>	0.3692	0.2926	0.3085	0.3168	0.2926	0.3086	0.3168
<i>s</i>	0.08049	0.06945	0.07194	0.07320	0.06945	0.07194	0.07320
Nuclear GTFs		${}^6\text{Li}$	${}^6\text{Li}$	${}^6\text{Li}$	${}^7\text{Li}$	${}^7\text{Li}$	${}^7\text{Li}$
Center (Å)							
<i>s</i>		0.000	0.000	0.000	0.000	0.000	0.000
Exponent							
<i>s</i>		578.785	578.795	578.799	628.419	628.429	628.434
Nuclear GTFs		H	D	T	H	D	T
Center (Å)							
<i>s</i>		1.663	1.686	1.604	1.662	1.685	1.603
<i>p</i>		1.674	1.667	1.619	1.673	1.667	1.618
Exponent							
<i>s</i>		18.483	27.130	33.802	18.484	27.131	33.802
<i>p</i>		20.220	27.365	33.772	20.222	27.366	38.772

the GTFs in the basis set is a very significant problem for molecular systems. It is noted that our Hartree–Fock energy (-7.961713 hartree) with only $8s$ GTFs gains 99.7 % of the total energy of near the Hartree–Fock limitation (-7.987352 hartree) with the $(15s11p5d/12s9p3d)$ [$11s11p5d/9s9p3d$] basis set [24].

When we used $1s$ $1p$ GTFs for the lithium nucleus, the LCGTF coefficient contribution of the nuclear $1p$ GTF essentially vanishes. This is why Table 4 shows only $1s$ GTF for the lithium nucleus. The $1s$ GTF exponent values for the ${}^6\text{Li}$ and the ${}^7\text{Li}$ nuclei are calculated to be 578.8 and 628.4, respectively. These values exhibit the extremely localized nuclear wave as compared with the hydrogen nucleus. This drastic increment of the exponent values is caused by not only the change in mass when changing from hydrogen to lithium nuclei but also by the change in charge from $+1$ to $+3$. It is regarded that the lithium nucleus can be approximated to a pure point charge; therefore the lithium nucleus is expressed with only a single s GTF under our approximation, and the LCGTF coefficient of the nuclear p GTF vanishes. The hydrogen nuclear GTFs in LiH are calculated to be more diffuse than

those in hydrogen molecules shown as the exponent values in Tables 2 and 4. The reason is considered to be due to the change in the electronic densities on the hydrogen nuclei between H_2 and LiH. In fact the number of electronic GTFs around the hydrogen nucleus in lithium hydride decreases compared with that in H_2 .

The change in the internuclear distance from ${}^6\text{LiH}$ to ${}^6\text{LiT}$ is 0.011 Å, which is almost identical to the case when changing from H_2 to HT. On the other hand, the ${}^6\text{Li}/{}^7\text{Li}$ isotope effect for the internuclear distance is negligibly small.

4.2 Energy component analysis

The Hartree–Fock energy, the relative energy, ΔE , the virial ratio, the dipole moment, the internuclear distance, R , and the energy components, T (T_e and T_n) and V (V_{ne} , V_{ee} , and V_{nn}), for each isotope species are summarized in Table 5. The energy lowering of the total energy from ${}^6\text{LiH}$ to ${}^7\text{LiT}$ is calculated to be 15.77 kcal/mol, which is shown as ΔE in Table 5. The energy change due to the

Table 5. Energy components analysis for lithium hydride and its isotopes using the [4s:1s1p] basis set with the DEMO method

	Point charge DEMO method						
	LiH	⁶ LiH	⁶ LiD	⁶ LiT	⁷ LiH	⁷ LiD	⁷ LiT
E_{HR} (hartree)	-7.961713	-7.763992	-7.773181	-7.777356	-7.775759	-7.784949	-7.789123
ΔE (kcal/mol)		0.00	-5.77	-8.39	-7.38	-13.15	-15.77
$(V/T) + 2$	-1.52E-07	1.00E-09	-1.10E-09	-1.30E-08	-2.01E-08	2.99E-08	6.60E-09
Dipole (a.u.)	2.389	2.390	2.394	2.395	2.389	2.392	2.394
R (Å) ^a	1.623	1.651	1.643	1.640	1.651	1.643	1.639
T (hartree)	7.961714	7.763992	7.773181	7.777356	7.775760	7.784949	7.789123
ΔT (kcal/mol)		0.00	5.77	8.39	7.38	13.15	15.77
T_e (hartree)	7.961714	7.669351	7.682647	7.688732	7.686595	7.699891	7.705977
ΔT_e (kcal/mol)		0.00	8.34	12.16	10.82	19.16	22.98
T_n (hartree)		0.079221 (⁶ Li)	0.079223 (⁶ Li)	0.079223 (⁶ Li)	0.073744 (⁷ Li)	0.073745 (⁷ Li)	0.073746 (⁷ Li)
ΔT_n (kcal/mol)		0.00	0.00	0.00	-3.44	-3.44	-3.44
T_n (hartree)		0.015420 (H)	0.011312 (D)	0.009400 (T)	0.015421 (H)	0.011312 (D)	0.009400 (T)
ΔT_n (kcal/mol)		0.00	-2.58	-3.78	0.00	-2.58	-3.78
V (hartree)	-15.923427	-15.527984	-15.546363	-15.554711	-15.551519	-15.569898	-15.578247
ΔV (kcal/mol)		0.00	-11.53	-16.77	-14.77	-26.30	-31.54
V_{ne} (hartree)	-20.354451	-19.888563	-19.920162	-19.934227	-19.914123	-19.945728	-19.959797
ΔV_{ne} (kcal/mol)		0.00	-19.83	-28.65	-16.04	-35.87	-44.70
V_{ee} (hartree)	3.452981	3.399021	3.407591	3.411333	3.400879	3.409452	3.413196
ΔV_{ee} (kcal/mol)		0.00	5.38	7.73	1.17	6.55	8.90
V_{nn} (hartree)	0.978042	0.961559	0.966209	0.968183	0.961725	0.966378	0.968354
ΔV_{nn} (kcal/mol)		0.00	2.92	4.16	0.10	3.02	4.26

^a Experimental values of the equilibrium internuclear distances of ⁷LiH and ⁷LiD are 1.5957 and 1.5941 Å, while those of average internuclear distances are 1.6074 and 1.6040 Å [23]

isotope effect between H/D and ⁶Li/⁷Li can be seen as the ΔE s between ⁶LiH and ⁶LiD (H/D) and between ⁶LiH and ⁷LiH (⁶Li/⁷Li), being -5.77 and -7.38 kcal/mol, respectively. In order to analyze the fact that the isotope effect on the total energy change for ⁶Li/⁷Li is greater than that for H/D, we have calculated the difference of each energy component change between ⁶LiH/⁶LiD (H/D) and ⁶LiH/⁷LiH (⁶Li/⁷Li).

The total kinetic energy changes, ΔT , of ⁶LiH/⁶LiD and ⁶LiH/⁷LiH are 5.77 and 7.38 kcal/mol, respectively, and these values have exactly the opposite sign to the total energy changes, ΔE , because of the virial theorem. The nuclear kinetic energy changes, ΔT_n of ⁶LiH/⁶LiD (H/D) and ⁶LiH/⁷LiH (⁶Li/⁷Li) are -2.58 and -3.44 kcal/mol, respectively. These changes show the same behavior as the total energy change, ΔE . Although the mass ratio between D and H is greater than that between ⁷Li and ⁶Li, the nuclear kinetic energy change of ⁶Li/⁷Li is larger than that for the H/D isotope effect. This arises from the difference in the charges between the lithium and the hydrogen nuclei. In the DEMO calculation, the nuclear MO is determined from the effective one-particle potential, as well as from the nuclear kinetic terms; therefore, the charge difference between the lithium and hydrogen nuclei affects the nuclear kinetic energy through the mean field from electrons and nuclei. Indeed, as shown in Sect. 4.1, the exponent of the lithium nuclear GTF becomes much greater than the hydrogen nuclear exponent, and this is not only due to the mass difference, but also to the charge difference between the hydrogen and the lithium nuclei.

On the other hand, the electronic kinetic energy changes, ΔT_e , of ⁶LiH/⁶LiD (H/D) and ⁶LiH/⁷LiH (⁶Li/⁷Li) are 8.34 and 10.82 kcal/mol, respectively. This means that the electron movement is more restricted from ⁶Li to ⁷Li than from H to D. This result is, in fact, observed in the optimized values of the electronic GTF exponents, where the change in the electronic GTF exponent between ⁶LiH/⁷LiH (⁶Li/⁷Li) is greater than that between ⁶LiH/⁶LiD (H/D).

The total potential energy changes, ΔV of ⁶LiH/⁶LiD and ⁶LiH/⁷LiH are -11.53 and -14.77 kcal/mol, respectively. The nuclear-electronic potential change, ΔV_{ne} , the electronic-electronic potential change, ΔV_{ee} , and the nuclear-nuclear potential change, ΔV_{nn} for ⁶LiH/⁶LiD are -19.83, 5.38, and 2.92 kcal/mol, respectively. On the other hand, ΔV_{ne} , ΔV_{ee} , and ΔV_{nn} for ⁶LiH/⁷LiH are -16.04, 1.17, and 0.10 kcal/mol. It is noted that ΔV_{ne} for ⁶LiH/⁶LiD (H/D) of -19.83 kcal/mol is larger than that for ⁶LiH/⁷LiH (⁶Li/⁷Li) of -16.04 kcal/mol. This is the reverse behavior compared to ΔE . In contrast the large ΔV_{ee} (5.38 kcal/mol) and the large ΔV_{nn} (2.92 kcal/mol) for ⁶LiH/⁶LiD show that the increase in the repulsive forces for H/D substitution is much larger than those for ⁶LiH/⁷LiH, ($\Delta V_{ee} = 1.17$ and $\Delta V_{nn} = 0.10$ kcal/mol). The repulsion changes, ΔV_{ee} and ΔV_{nn} of ⁶Li/⁷Li turn out to be small compared to those of H/D, since these three energy components, ΔV_{ne} , ΔV_{ee} , and ΔV_{nn} , are directly related to the internuclear distance between lithium and hydrogen.

Consequently we found that the total energy change between ⁶Li/⁷Li is greater than that between H/D, since ΔV_{ee} and ΔV_{nn} of ⁶Li/⁷Li are smaller than those of H/D.

5 Concluding remarks

The DEMO method can determine both the nuclear and the electronic wave functions simultaneously. We have applied the DEMO method to the hydrogen and lithium hydride molecules, and have analyzed each energy component within the Hartree–Fock approximation. The present study clearly confirms the H/D/T and ${}^6\text{Li}/{}^7\text{Li}$ isotope effect on internuclear distance, nuclear and electronic wave functions, and each energy component.

In the case of the hydrogen isotope molecule, the nuclear–electronic potential component becomes more stable as the nuclear mass increases from proton to triton, as does the nuclear kinetic component. This gives the result that the total energy decreases as the nuclear mass increases.

In the case of lithium hydride, the isotope effect on the total energy change for ${}^6\text{Li}/{}^7\text{Li}$ is larger than that for H/D. The reason is considered to be due to the electronic–electronic and nuclear–nuclear repulsion changes, which are smaller for ${}^6\text{Li}/{}^7\text{Li}$ than for H/D, as well as the nuclear kinetic component change.

It would be a more interesting subject to study the many-body effect, such as the electronic–nuclear and nuclear–nuclear correlation effects, as well as the electron–electron correlation, which is not treated in the present Hartree–Fock DEMO calculation.

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