Some accurate nonadditive multipolar interaction constants for three hydrogen atoms

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Momentum-space two-body perturbation wave functions are applied to an accurate evaluation of the nonadditive three-body interaction among well-separated three hydrogen atoms.

It is known[1] that even for the case of long-range (van der Waals) interactions among well-separated atoms, the total interaction energy of more than two atoms is not equal to the sum of pairwise interaction energies and the nonadditive three-body term often gives a significant contribution. Axilrod and Teller[2] derived the explicit expression for the leading nonadditive energy, the dipole-dipole-dipole term, and its importance has been thereafter referred to frequently in connection with the properties of rare-gas crystals and atom clusters.

In the present paper, we apply the recently reported momentum-space perturbation wave function for the H(1*s*)-H(1*s*) van der Waals system[3,4] to the *direct* and *reliable* evaluation of the nonadditive three-body interaction in the H(1*s*)-H(1*s*)-H(1*s*) systems.

For the well-separated three ground-state hydrogen atoms, the nonadditive three-body energy appears in the third order of the perturbation and can be written as

$$E_{\rm III}^{(3)}=2[\langle 1s(2)\psi^{(1)}(3,1)|V^{(1)}(1,2)|1s(1)\psi^{(1)}(2,3)\rangle + \langle 1s(3)\psi^{(1)}(1,2)|V^{(1)}(2,3)|1s(2)\psi^{(1)}(3,1)\rangle + \langle 1s(1)\psi^{(1)}(2,3)|V^{(1)}(3,1)|1s(3)\psi^{(1)}(1,2)\rangle] , \quad (1)$$

since the three-body potential $V^{(1)}(1,2,3)$ is the sum of the two-body potentials $V^{(1)}(i,j)$. $\psi^{(1)}(i,j)$ is the first-order wave function[3,4] for the *two* hydrogen atoms i and j.

When the multipole expansion is applied to $V(i,j)$, $V(i,j)$ and $\psi^{(1)}(i,j)$ are developed as a power series of the reciprocal internuclear distance R_{ij}^{-1}, and their individual coefficients are specified by two hydrogenic azimuthal quantum numbers l and l'.[3,4] Then the three-body interaction energy $E_{\rm III}^{(3)}$ is expressed as

$$\begin{aligned} E_{\rm III}^{(3)} = & Z_{111}W_{111}+Z_{112}(W_{112}+W_{121}+W_{211}) \\ & +Z_{113}(W_{113}+W_{131}+W_{311}) \\ & +Z_{122}(W_{122}+W_{212}+W_{221}) \\ & +Z_{222}W_{222}+\cdots , \end{aligned} \quad (2)$$

where $Z_{ll'l''}$ is the interaction constant arising from the radial part of $\psi^{(1)}(i,j)$, and $\cdots$ represents higher-order interactions, while the geometrical factor $W_{ll'l''}$ comes from the angular part of $\psi^{(1)}(i,j)$ including the internuclear distances. Note that the terms on the right-hand side of Eq. (2) represent the ***DDD***, ***DDQ***, ***DDO***, ***DQQ***, and ***QQQ*** interactions, respectively, where ***D***, ***Q***, and ***O*** mean dipole, quadrupole, and octupole contributions.

The evaluation of the geometrical factor $W_{ll'l''}$ needs the rotation $\mathcal{R}$ of the spherical harmonics, since Y_{lm}'s involved in the two-body function $\psi^{(1)}(i,j)$ are defined in the local coordinate system where the z axis is taken along the internuclear vector $\mathbf{R}_{ij}$ $(=\mathbf{R}_j-\mathbf{R}_i)$ for each pair of atoms i and j. The rotational relation is given by[5]

$$\mathcal{R}(\alpha,\beta,\gamma)Y_{lm}=\sum_{m'=-l}^{+l} Y_{lm'}D_{m'm}^{(l)}(\alpha\beta\gamma) , \quad (3a)$$

$$D_{m'm}^{(l)}(\alpha\beta\gamma)=\exp(-i\alpha m')d_{m'm}^{(l)}(\beta)\exp(-i\gamma m) , \quad (3b)$$

$$d_{m'm}^{(l)}(\beta)=[(l+m')!(l-m')!(l+m)!(l-m)!]^{1/2}\sum_s(-1)^{m'-m+s}[(l+m-s)!(l-m'-s)!s!(m'-m+s)!]^{-1} \times[\cos(\beta/2)]^{2l+m-m'-2s}[\sin(\beta/2)]^{m'-m+2s} , \quad (3c)$$

where s runs over all integers for which the factorials are meaningful.

Our final results for the geometrical factors W_{111}, W_{112}, W_{122}, and W_{222} agree with the known results[6] except for some constant factors which are absorbed in the interaction constants. The explicit form for W_{113},

$$W_{113}=-(\tfrac{5}{192})R_{12}^{-3}R_{23}^{-5}R_{31}^{-5}\{[9+8\cos(2C)-49\cos(4C)]-6\cos(A-B)[9\cos C+7\cos(3C)]\}\ , \tag{4}$$

is newly derived in this study, where A, B, and C ($A+B+C=\pi$) are the three internal angles of the triangle of the hydrogen atoms. (Note that the expressions for W_{131}, etc. are obtained by the cyclic permutation of the distances and angles.)

After some manipulations, the nonadditive three-body interaction constants $Z_{ll'l''}$, appearing in Eq. (2), have been found to be

$$Z_{111}=-8\sum_{n,n',m,m'=2} b_{nn'}^{(3)}b_{mm'}^{(3)}I_{n'}^{1}I_{m}^{1}J_{nm'}^{1}\ , \tag{5a}$$

$$Z_{112}=(\tfrac{8}{3})\sum_{n,m=3}\sum_{n',m'=2} b_{nn'}^{(4)}b_{mm'}^{(4)}I_{n'}^{1}I_{m'}^{1}J_{nm}^{2} +(16/\sqrt{5})\sum_{n,n',m'=2}\sum_{m=3} b_{nn'}^{(3)}b_{mm'}^{(4)}I_{n'}^{1}I_{m}^{2}J_{nm'}^{1}\ , \tag{5b}$$

$$Z_{113}=-(\tfrac{8}{3})\sum_{n,m=4}\sum_{n',m'=2} b_{nn'}^{(5b)}b_{mm'}^{(5b)}I_{n'}^{1}I_{m'}^{1}J_{nm}^{3} -(16\sqrt{14}/7)\sum_{n,n',m'=2}\sum_{m=4} b_{nn'}^{(3)}b_{mm'}^{(5b)}I_{n'}^{1}I_{m}^{3}J_{nm'}^{1}\ , \tag{5c}$$

$$Z_{122}=-(\tfrac{8}{5})\sum_{n,m=3}\sum_{n',m'=2} b_{nn'}^{(4)}b_{mm'}^{(4)}I_{n}^{2}I_{m}^{2}J_{n'm'}^{1} -(16/\sqrt{5})\sum_{n,m,m'=3}\sum_{n'=2} b_{nn'}^{(4)}b_{mm'}^{(5a)}I_{n'}^{1}I_{m}^{2}J_{nm'}^{2}\ , \tag{5d}$$

$$Z_{222}=(\tfrac{24}{5})\sum_{n,n',m,m'=3} b_{nn'}^{(5a)}b_{mm'}^{(5a)}I_{n'}^{2}I_{m}^{2}J_{nm'}^{2}\ , \tag{5e}$$

where $\{b_{nn'}^{(k)}\}$ are the coefficients appearing in the radial part of the two-body perturbation wave function $\psi^{(1)}(i,j)$,[3,4] and

$$I_{n}^{k}=2^{-k-1}\sqrt{(k+1)(2k+1)!}(\delta_{n,k+1}+\sqrt{2k+4}\,\delta_{n,k+2})\ , \tag{6a}$$

$$J_{nm}^{k}=a_{-}(n,k)\delta_{n,m+1}+\delta_{nm}+a_{+}(n,k)\delta_{n,m-1}\ , \tag{6b}$$

$$a_{-}(n,k)=(\tfrac{1}{2})\sqrt{(n+k)(n-k-1)/n(n-1)}\ , \tag{6c}$$

$$a_{+}(n,k)=(\tfrac{1}{2})\sqrt{(n-k)(n+k+1)/n(n+1)}\ , \tag{6d}$$

which result from the radial integrals involving the associated Laguerre function.

Convergent values for the five types of interaction constants of the hydrogenic three-body interactions are (in atomic units):

$$Z_{111}=-7.214\,154\,84,\quad Z_{112}=78.707\,166\,4,\quad Z_{113}=-1424.065\,96\ ,$$
$$Z_{122}=-289.371\,191,\quad Z_{222}=359.157\,930\ ,$$

when 55-term expansion is applied to $\psi^{(1)}(i,j)$. These values are considerably accurate and reliable than those in the literature.[6,7] The characteristic of the present values is that they have been determined *directly* from the perturbation wave functions analytically and explicitly obtained in momentum space. These interaction constants should be compared with the very recent elaborate work[8,9] based on the pseudostate method.

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