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PAIRWISE NONADDITIVE DISPERSION POTENTIAL FOR ASYMMETRIC MOLECULES

Daniel E. Stogryn
Douglas Advanced Research Laboratories, Huntington Beach, California 92647
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The form of the pairwise nonadditive three-body dispersion potential for asymmetric molecules is derived. It is found that molecular asymmetry can have a large influence on interactions of this type. An example indicating the possible use of these results in understanding cohesive energies in crystals is given.

The work of Muto,[1] Axilrod and Teller,[2] and Midzuno and Kihara[3] on three-body pairwise nonadditive dispersion interactions between spherically symmetric molecules is extended to the case of molecules of arbitrary asymmetry.

Consider three neutral molecules α, β, and γ, which are not necessarily identical, in nondegenerate ground states. The perturbation to the sum of the free-molecule Hamiltonians is, in the dipole approximation,

$$V=V_{\alpha\beta}+V_{\alpha\gamma}+V_{\beta\gamma}, \tag{1}$$

with

$$V_{\alpha\beta}=\mu_{\alpha i}(T_{\alpha\beta})_{ij}\mu_{\beta j}, \tag{2}$$

where $\mu_{\alpha i}$ is the ith component of the dipole-moment operator for molecule α and $(T_{\alpha\beta})_{ij}$ is the ij component of the interaction tensor between molecules α and β. This tensor is defined by the equation

$$(T_{\alpha\beta})_{ij}=-r_{\alpha\beta}^{-3}[3(e_{\alpha\beta})_i(e_{\alpha\beta})_j-\delta_{ij}], \tag{3}$$

where $r_{\alpha\beta}$ is the separation between molecules α and β, and $(e_{\alpha\beta})_i$ is the ith component of a unit vector pointing from molecule α towards molecule β. (Here, and elsewhere in this paper, Latin letter subscripts denote vector or tensor components, while Greek letter subscripts refer to molecules.)

The pairwise nonadditive dispersion energy W is given, according to third-order Rayleigh-Schrödinger perturbation theory, by

$$\begin{aligned}W=2\Bigg[&\sum\frac{\langle g(\alpha)g(\beta)|V_{\alpha\beta}|n(\alpha)n(\beta)\rangle\langle n(\alpha)g(\gamma)|V_{\alpha\gamma}|g(\alpha)n(\gamma)\rangle\langle n(\beta)n(\gamma)|V_{\beta\gamma}|g(\beta)g(\gamma)\rangle}{[E(n(\alpha))+E(n(\beta))][E(n(\beta))+E(n(\gamma))]}\\&+\sum\frac{\langle g(\alpha)g(\beta)|V_{\alpha\beta}|n(\alpha)n(\beta)\rangle\langle n(\beta)g(\gamma)|V_{\beta\gamma}|g(\beta)n(\gamma)\rangle\langle n(\alpha)n(\gamma)|V_{\alpha\gamma}|g(\alpha)g(\gamma)\rangle}{[E(n(\alpha))+E(n(\beta))][E(n(\alpha))+E(n(\gamma))]}\\&+\sum\frac{\langle g(\alpha)g(\gamma)|V_{\alpha\gamma}|n(\alpha)n(\gamma)\rangle\langle n(\alpha)g(\beta)|V_{\alpha\beta}|g(\alpha)n(\beta)\rangle\langle n(\beta)n(\gamma)|V_{\beta\gamma}|g(\beta)g(\gamma)\rangle}{[E(n(\alpha))+E(n(\gamma))][E(n(\beta))+E(n(\gamma))]}\Bigg],\end{aligned} \tag{4}$$

where $g(\alpha)$ denotes the ground state of molecule α, $n(\alpha)$ the nth excited state of molecule α, and $E(n(\alpha))$ the energy difference between states $n(\alpha)$ and $g(\alpha)$. The summations extend over all values of $n(\alpha)$, $n(\beta)$, and $n(\gamma)$. Equation (4) is readily put in the form

$$W=4(T_{\alpha\beta})_{ij}(T_{\alpha\gamma})_{kl}(T_{\beta\gamma})_{mn}\sum D\langle g(\alpha)|\mu_{\alpha i}|n(\alpha)\rangle\langle n(\alpha)|\mu_{\alpha k}|g(\alpha)\rangle\langle g(\beta)|\mu_{\beta j}|n(\beta)\rangle\langle n(\beta)|\mu_{\beta m}|g(\beta)\rangle \times\langle g(\gamma)|\mu_{\gamma l}|n(\gamma)\rangle\langle n(\gamma)|\mu_{\gamma n}|g(\gamma)\rangle, \tag{5}$$

where

$$D=\frac{E(n(\alpha))+E(n(\beta))+E(n(\gamma))}{[E(n(\alpha))+E(n(\beta))][E(n(\alpha))+E(n(\gamma))][E(n(\beta))+E(n(\gamma))]}. \tag{6}$$

Now, following Unsöld[4] and, even more closely, the procedure of Buckingham[5] in their treatments of second-order perturbation effects, we approximate D by the equation

$$D=\frac{(U_\alpha+U_\beta+U_\gamma)U_\alpha U_\beta U_\gamma}{(U_\alpha+U_\beta)(U_\alpha+U_\gamma)(U_\beta+U_\gamma)E(n(\alpha))E(n(\beta))E(n(\gamma))}, \tag{7}$$

where U_α is some characteristic energy for molecule α. (This step implies that the characteristic energies corresponding to the three principal directions of the polarizability tensor of a molecule are equal. In the study of two-body dispersion energies, this assumption is frequently made.[5,6]) If, furthermore, the U's are taken to be exactly the same quantities which occur in Ref. 5 in the treatment of two-body dispersion forces between asymmetric molecules, we may write

$$C_{\alpha\beta}=3U_\alpha U_\beta\bar{\alpha}_\alpha\bar{\alpha}_\beta/2(U_\alpha+U_\beta),\quad C_{\alpha\gamma}=3U_\alpha U_\gamma\bar{\alpha}_\alpha\bar{\alpha}_\gamma/2(U_\alpha+U_\gamma),\quad C_{\beta\gamma}=3U_\beta U_\gamma\bar{\alpha}_\beta\bar{\alpha}_\gamma/2(U_\beta+U_\gamma), \tag{8}$$

with $C_{\alpha\beta}$ the magnitude of the coefficient of the spherically symmetric component of the $r_{\alpha\beta}^{-6}$ second-order two-body dispersion energy, and $\bar{\alpha}_\alpha$, the mean polarizability, being one third the trace of the polarizability tensor of molecule α. Equations (8) can be inverted to give the U's in terms of the C's. We then find

$$\frac{(U_\alpha+U_\beta+U_\gamma)U_\alpha U_\beta U_\gamma}{(U_\alpha+U_\beta)(U_\alpha+U_\gamma)(U_\beta+U_\gamma)}=\frac{2\nu_{\alpha\beta\gamma}}{3\bar{\alpha}_\alpha\bar{\alpha}_\beta\bar{\alpha}_\gamma}, \tag{9}$$

where

$$\nu_{\alpha\beta\gamma}=\frac{2R_\alpha R_\beta R_\gamma(R_\alpha+R_\beta+R_\gamma)}{(R_\alpha+R_\beta)(R_\alpha+R_\gamma)(R_\beta+R_\gamma)}, \tag{10}$$

and

$$\begin{aligned}R_\alpha^{-1}&=(C_{\alpha\beta}\bar{\alpha}_\gamma)^{-1}+(C_{\alpha\gamma}\bar{\alpha}_\beta)^{-1}-(C_{\beta\gamma}\bar{\alpha}_\alpha)^{-1},\\ R_\beta^{-1}&=(C_{\beta\gamma}\bar{\alpha}_\alpha)^{-1}+(C_{\alpha\beta}\bar{\alpha}_\gamma)^{-1}-(C_{\alpha\gamma}\bar{\alpha}_\beta)^{-1},\\ R_\gamma^{-1}&=(C_{\alpha\gamma}\bar{\alpha}_\beta)^{-1}+(C_{\beta\gamma}\bar{\alpha}_\alpha)^{-1}-(C_{\alpha\beta}\bar{\alpha}_\gamma)^{-1}.\end{aligned} \tag{11}$$

Thus, on using the well-known quantum mechanical expression[5] for the components of the polarizability tensor $(\alpha_\alpha)_{ij}$, Eq. (5) becomes

$$W=\frac{\nu_{\alpha\beta\gamma}}{3\bar{\alpha}_\alpha\bar{\alpha}_\beta\bar{\alpha}_\gamma}(T_{\alpha\beta})_{ij}(T_{\alpha\gamma})_{kl}(T_{\beta\gamma})_{mn}(\alpha_\alpha)_{ik}(\alpha_\beta)_{jm}(\alpha_\gamma)_{ln}. \tag{12}$$

In the special case of spherical molecules, Eq. (12) reduces to the result, derived by means of a variational calculation, found by Midzuno and Kihara.[3]

The application of Eq. (12) to the analysis of third virial coefficients of gases composed of asymmetric molecules is described elsewhere.[7] Here, we wish to indicate a possible use of Eq. (12) in understanding cohesive energies and structures of molecular crystals. According to Eq. (12), there is a strong dependence of the pairwise nonadditive three-body dispersion energy on the relative orientations of the three molecules. To give a simple quantitative demonstration of this, consider the case of three identical linear moledules with centers positioned on a straight line as shown in Fig. 1. In case 1, the axes of the two end molecules are aligned with the line joining centers, while in case 2

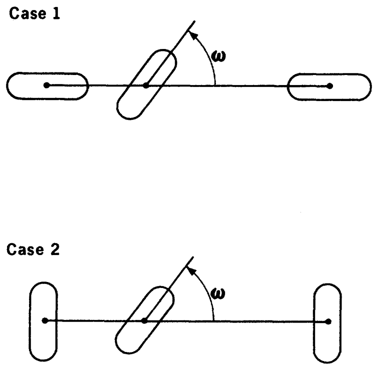

FIG. 1. The two orientations for a group of three molecules whose relative energies are shown in Fig. 2.

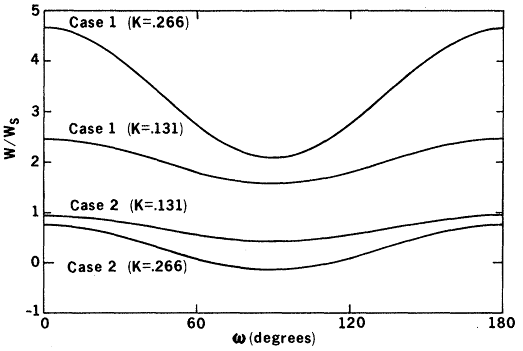

FIG. 2. A plot of the relative three-body dispersion energies of linear molecules compared with spherically symmetric molecules for two values of κ, the polarizability anisotropy.

the axes are perpendicular to this line and parallel to the plane of the figure. In both cases, the middle molecule is allowed to rotate in the plane of the figure making an angle ω with the line joining centers. The polarizability tensor of a linear molecule can be described by two constants: $\overline{\alpha}$ and the anisotropy[8,5] κ. If W_S denotes the special form of Eq. (12) when the three molecules are spherical and with the same mean polarizabilities as in the case of the linear molecules, we find

$$W/W_S = 1 + \tfrac{9}{2}\kappa - \tfrac{11}{2}\kappa^3 + \tfrac{3}{2}\kappa(3 + 10\kappa + 11\kappa^2)\cos^2\omega$$

for case 1, and

$$W/W_S = 1 + \tfrac{3}{2}\kappa^2 - \tfrac{5}{2}\kappa^3 - \tfrac{9}{2}\kappa\sin^2\omega - 6\kappa^2(1-\kappa)\cos^2\omega$$

for case 2. A plot of these functions is given in Fig. 2 where the values of κ correspond to those for CO_2 ($\kappa = 0.266$) and N_2 ($\kappa = 0.131$). Thus, rather large changes in the pairwise nonadditive three-body dispersion energy can occur for anisotropic molecules compared with the case of spherical molecules. For case 2 ($\kappa = 0.266$), there is even a change from an attractive interaction in the case of spherical molecules to a repulsive interaction for the linear molecules when ω is between 66 and 114 degrees. Calculations of this type with appropriate descriptions of molecular asymmetry and orientations can have a bearing on the understanding of the cohesive energy of ice or other crystals.

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