

The $S(^1D) + H_2(X^1\Sigma_g^+)$ interaction: long-range multipolar potentials

I. LONG-RANGE ELECTROSTATIC ENERGIES

The electrostatic interaction between the permanent quadrupole moments of $S(^1D)$ and $H_2(X^1\Sigma_g^+)$ can be written as a 5×5 potential matrix

$$V_{\lambda,\lambda'}^{\text{elec}}(R, \theta) = \frac{1}{R^5} C_5^{\lambda\lambda'} C_{2,\lambda'-\lambda}(\theta, 0), \quad (1)$$

where $\lambda = 0, \pm 1, \pm 2$ is the projection of the atomic orbital angular momentum \mathbf{L} along the BF z -axis. According to Eq. 14 of the Appendix and the use of the Wigner-Eckart theorem, the electrostatic coefficients $C_5^{\lambda\lambda'}$ take simple forms in terms of the atomic and diatomic quadrupole moments, $\Theta_A = \langle L0 | \hat{Q}_{20}^{(A)} | L0 \rangle$ and $\Theta_B = \langle 0 | \hat{Q}_{20}^{(B)} | 0 \rangle$, respectively. For convenience, we report in Table I the analytical forms of the 5×5 electrostatic coefficients $C_5^{\lambda\lambda'}$ in terms of the product $\Theta_A \Theta_B$. The numerical results given in Table I correspond to the computed value $\Theta_A = +2.075$ a.u. for $S(^1D)$ (details of the calculation are given in Sec. III-B) and the value $\Theta_B = +0.481$ a.u. selected from the literature [1] for H_2 .

TABLE I: Long-range non-zero electrostatic coefficients $C_5^{\lambda\lambda'}$ (in atomic units) for the $S(^1D) + H_2(X^1\Sigma_g^+)$ interaction.

λ	λ'	$C_5^{\lambda\lambda'}$ (analytic)	$C_5^{\lambda\lambda'}$
0	0	$6 \Theta_A \Theta_B$	5.988
± 1	± 1	$3 \Theta_A \Theta_B$	2.994
± 2	± 2	$-6 \Theta_A \Theta_B$	-5.988
0	± 1	$-2 \Theta_A \Theta_B$	-1.996
0	± 2	$-1 \Theta_A \Theta_B$	-0.998
± 1	0	$2 \Theta_A \Theta_B$	1.996
± 1	∓ 1	$-\sqrt{3/2} \Theta_A \Theta_B$	-1.222
± 1	± 2	$-2\sqrt{6} \Theta_A \Theta_B$	-4.889
± 2	0	$-1 \Theta_A \Theta_B$	-0.998
± 2	± 1	$2\sqrt{6} \Theta_A \Theta_B$	4.889

II. LONG-RANGE DISPERSION ENERGIES

The dispersion interaction between the dipole-induced moments of $S(^1D)$ and $H_2(X^1\Sigma_g^+)$ can also be written as a 5×5 potential matrix

$$V_{\lambda,\lambda'}^{\text{disp}}(R, \theta) = -\frac{1}{R^6} \sum_{k=0,2} C_{6,k}^{\lambda\lambda'} C_{k,\lambda'-\lambda}(\theta, 0), \quad (2)$$

where $C_{6,0}^{\lambda\lambda'}$ and $C_{6,2}^{\lambda\lambda'}$ are the isotropic and anisotropic dispersion coefficients, respectively. According to Eqs. 16 and 17 of the Appendix and the use of the Wigner-Eckart theorem, the whole set of dispersion coefficients can be derived from the knowledge of the parallel and perpendicular components of the dynamic dipole polarizabilities associated with H_2 and each atomic substate of definite symmetry. The results given in Table II correspond to the computed values of the dynamic polarizabilities for $S(^1D)$ (see details in Sec. III-B) and the values selected from the literature [2] for H_2 .

TABLE II: Long-range non-zero dispersion coefficients $C_{6,k}^{\lambda\lambda'}$ (in atomic units) for the $S(^1D) + H_2(X^1\Sigma_g^+)$ interaction.

λ	λ'	k	$C_{6,k}^{\lambda\lambda'}$
0	0	0	38.897
± 1	± 1	0	39.618
± 2	± 2	0	41.779
0	0	2	3.668
± 1	± 1	2	3.907
± 2	± 2	2	4.625
0	± 1	2	0.159
0	± 2	2	0.159
± 1	0	2	-0.159
± 1	∓ 1	2	0.195
± 1	± 2	2	0.391
± 2	0	2	0.159
± 2	± 1	2	-0.391

- [1] D. Spelsberg, T. Lorenz, and W. Meyer, *J. Chem. Phys.* **99**, 7845 (1993).
[2] D. M. Bishop and J. Pipin, *J. Chem. Phys.* **97**, 3375 (1992).