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SPIN-SPIN INTERACTION FOR VERY LARGE ATOMIC SEPARATIONS*†

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In considerations of very long range interactions between atoms or molecules, the interaction of permanent magnetic or electrostatic multipole moments seems to have been overlooked. In some cases the permanent multipole interactions give rise to the lead term in the $1/R$ expansion of the interaction energy (where R is the intermolecular separation).

Thus, the principal contributions to the energy of interaction of two ground-state hydrogen atoms at separations greater than 50 Å is due to the spin-dipole-spin-dipole interaction energy which varies as R^{-3} , rather than the dispersion energy which varies between R^{-6} and R^{-7} . While the dispersion energy is weakened by retardation effects as R increases, the magnetic or electrostatic permanent-moment-permanent-moment interactions are not retarded.

Consider the interaction of two ground-state hydrogen atoms separated by a distance R (energy and length in atomic units). For moderately large separations where the charge distributions of the two atoms do not overlap and $R < \chi_0$, where χ_0 is the reduced wavelength characteristic of the important transition dipole matrix elements occurring in the dispersion energy, the interaction energy can be calculated by using the Breit-Pauli approximation for the relativistic interaction Hamiltonian.^{1,2} The result for the interaction energy through $O(\alpha^2/R^6)$, where $\alpha \sim 1/137$ is the fine structure

constant, is given by³

$$\mathcal{E}_{ab} = \frac{A\alpha^2}{R^3} + \frac{0.40\alpha^2}{R^4} - \frac{6.50}{R^6} + \dots, \quad (1)$$

where $A = 0$ for the $^1\Sigma$ state of the system, $A = 1$ for the $^3\Sigma$ state with $M_S = 0$, and $A = -\frac{1}{2}$ for the $^3\Sigma$ states with $M_S = \pm 1$ (M_S is the projection of the total spin of the system on the interatomic axis). Here $A\alpha^2/R^3$ is the spin-dipole interaction energy; $-6.50/R^6$ is the usual London dispersion energy⁴; and $0.40\alpha^2/R^4$ is a relativistic correction^{1,5} to the London energy. From either the stationary state⁶ or the S -matrix⁷ covariant quantum-electrodynamic calculations of the interaction energy, it appears that the permanent spin-dipole-spin-dipole interaction energy is not retarded^{2,8} and therefore does not change its functional dependence⁹ when $R \gtrsim \chi_0$. Thus at very large separations, $R > \chi_0$, the energy of interaction of two ground-state hydrogen atoms should have the form

$$\mathcal{E}_{ab} = \frac{A\alpha^2}{R^3} - \frac{37}{\alpha R^7} + \dots, \quad (2)$$

where $-37(\alpha R^7)^{-1}$ is the Casimir and Polder¹⁰ retarded dispersion energy. For the $^3\Sigma$ states the spin-dipole interaction energy dominates for large separations.

The values of R for which the magnitude of the spin-dipole-spin-dipole interaction energy equals the magnitude of the dispersion en-

ergy can easily be calculated. Using¹¹ Eq. (1), the magnitudes of the two interaction energies become equal at $R \sim 50 \text{ \AA}$ for the $^3\Sigma_{\pm 1}$ states of the hydrogen molecule.

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¹W. J. Meath and J. O. Hirschfelder, *J. Chem. Phys.* **44**, 3197, 3210 (1966).

²L. Gomberoff and E. A. Power, to be published.

³W. J. Meath, to be published.

⁴F. London, *Z. physik. Chem (Leipzig)* **B11**, 222 (1930); *Trans. Faraday Soc.* **33**, 8 (1937).

⁵See also E. A. Power and S. Zienau, *J. Franklin Inst.* **263**, 403 (1957). There is also an $O(\alpha^2/R^6)$ relativistic energy which is omitted here since it is of $O(\alpha^2)$ smaller than the London dispersion energy [see Ref. 3]. There is also an R^{-5} term which has a factor α^6 and which is also omitted as it is very small.

⁶See for example, R. R. McLone and E. A. Power, *Mathematika* **11**, 91 (1964); *Proc. Roy. Soc. (London)* **286**, 573 (1965); D. W. Condiff, University of Wisconsin Theoretical Chemistry Institute Report No. WIS-TCI-155, 25 May 1966 (unpublished).

⁷See for example, M. J. Stephen, *J. Chem. Phys.* **40**, 669 (1964); and Ref. 2.

⁸Also, for example, taking the limit as $\chi_0 \rightarrow \infty$ of the electrostatic resonance energy of McLone and Power⁶ or Stephen⁷ yields an unretarded dipole-interaction energy.

⁹At extremely large distances the hyperfine splitting begins to retard the spin-spin forces. However, the wavelength χ_0 is not involved, and in the normally so-called retardation region (macroscopic distances $>R \gtrsim \chi_0$), the spin-spin potential is not changed in its functional form from its value in the near zone (atomic distances $<R \lesssim \chi_0$).

¹⁰H. B. G. Casimir and D. Polder, *Phys. Rev.* **73**, 360 (1948).

¹¹It should be pointed out that for $R \sim \chi_0$ the dispersion energy cannot be expanded in powers of $1/R$, and the exact quantum electrodynamic result of Ref. 10 must be used. However, using the data of Ref. 1, it is easy to show that the spin-dipole energy and the dispersion energy become equal at a value of R for which Eq. (1) represents the interaction energy very accurately.

THRESHOLD BEHAVIOR OF THE $n = 2$ EXCITATION CROSS SECTION IN ATOMIC HYDROGEN*

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In this communication we report new results in the behavior of the $n = 2$ excitation cross sections in atomic hydrogen for incident electron energies smaller than the $n = 4$ threshold. Because of the continuing lack of agreement between theory and experiment in this, one of the most simple atomic scattering problems,¹ we have attempted to clarify the situation by solving the electron-hydrogen-atom Schrödinger equation using the close-coupling^{2,3} method with the inclusion of all the first six ($1s$ through $3d$) eigenstates of atomic hydrogen. The results, compared in Figs. 1 and 2 with those of previous,⁴ more restricted calculations, show a num-

ber of important features which we now discuss.⁵

We first notice the rapid decrease in the excitation cross sections which sets in at the energy of resonances (which we find and discuss below) occurring just below the $n = 3$ threshold and leads to a divergence between the two sets of results at higher energies. At the same time, for energies below those at which the effects of the $n = 3$ states become noticeable, there is little difference between the two approximations. This effect is noticeable in all partial waves, and we believe on the basis of these results that the close-coupling expansion is reliable up to an energy corresponding to the thresholds,