MULTIPOLE EXPANSION OF THE RETARDED INTERATOMIC POTENTIAL ENERGY: DERIVATION FROM RELATIVISTIC ELECTRON THEORY

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The inductive and dispersive retarded interaction energies of two ground state hydrogen atoms described by Dirac theory are obtained up to all multipole orders. The long range terms are given as symmetric expressions in the electric and magnetic dipole moments.

The multipole expansion of the retarded interaction energy of two atoms in their ground states has been derived recently [1] on the basis of nonrelativistic quantum electrodynamics. In this letter the potential energy $V(R)$ of two relativistic ground state hydrogen atoms at a distance R will be given. Details of the calculations will be published elsewhere.

From the scattering matrix $S_{\mathrm{fi}} = \delta_{\mathrm{fi}} - 2\pi\mathrm{i}\delta(E_{\mathrm{f}} - E_{\mathrm{i}})V_{\mathrm{fi}}$ for two atoms with fixed nuclei $V(R)$ follows as the part of V_{00} that depends on the separation R. Up to fourth order perturbation theory $V(R)$, averaged over the ground states of both atoms independently, results from the two photon exchange contributions only. The inductive part, with ground level intermediate states for one of the atoms, is found as:

$$V_{\mathrm{ind}}(R) = -\frac{1}{g_{\mathrm{a}}g_{\mathrm{b}}} \sum_{\alpha_0\beta_0\alpha\beta}{}' \frac{\Gamma^0_{\alpha_1}\Gamma^0_{\beta_1}\Gamma^{0*}_{\alpha_2}\Gamma^{0*}_{\beta_2} + \boldsymbol{\Gamma}_{\alpha_1}\cdot\boldsymbol{\Gamma}_{\beta_1}\boldsymbol{\Gamma}^*_{\alpha_2}\cdot\boldsymbol{\Gamma}^*_{\beta_2}}{16\pi^2 k_\alpha R_1 R_2} + (\alpha \leftrightarrow \beta) \tag{1}$$

where the atomic states of atoms a and b are labelled α and β, and in particular the ground states (with orders of degeneracy g_{a} and g_{b}) α_0 and β_0; the prime at the summation sign limits α and β to the states with $k_\alpha \equiv E_\alpha - E_{\alpha_0} \neq 0$, $k_\beta = 0$. The matrix elements $\Gamma^\mu_{\alpha i} \equiv -e\langle\alpha_0|\gamma^0\gamma^\mu \exp(-\boldsymbol{r}\cdot\boldsymbol{\nabla}_i) - g^{0\mu}|\alpha\rangle$ (with $\boldsymbol{r}$ the electron coordinate relative to the nucleus) may be expressed in terms of the relativistic electric and magnetic multipole moments $\mu^n_\alpha \equiv -e\langle\alpha_0|\boldsymbol{r}^n|\alpha\rangle/n!$ and $\nu^n_\alpha \equiv -e\langle\alpha_0|\boldsymbol{r}^{n-1}\boldsymbol{r}\times\gamma^0\boldsymbol{\gamma}|\alpha\rangle n/(n+1)!$ as:

$$\Gamma^0_{\alpha i} = \sum_{n=1}^{\infty} (-\boldsymbol{\nabla}_1)^n \vdots\, \mu^n_\alpha, \qquad \boldsymbol{\Gamma}_{\alpha i} = \sum_{n=1}^{\infty} (-\boldsymbol{\nabla}_i)^{n-1} \vdots\, (\mathrm{i}k_\alpha \mu^n_\alpha + \nu^n_\alpha \times \boldsymbol{\nabla}_i) \ . \tag{2}$$

After the differentiations with respect to $\boldsymbol{R}_1$ and $\boldsymbol{R}_2$ in eq. (1) have been performed these vectors are to be put equal to $\boldsymbol{R} = \boldsymbol{R}_{\mathrm{b}} - \boldsymbol{R}_{\mathrm{a}}$. Taking the nonrelativistic limit of (2) by means of a Foldy-Wouthuysen transformation we recover from (1) the results of paper IV. The leading term of the expansion of $V_{\mathrm{ind}}(R)$ in powers of R^{-1} reads in terms of the relativistic electric and magnetic dipole matrix elements:

$$V^{\mathrm{L}}_{\mathrm{ind}}(R) = -\frac{1}{g_{\mathrm{a}}g_{\mathrm{b}}} \sum_{\alpha_0\beta_0\alpha\beta}{}' \frac{|\mu^1_\alpha|^2|\mu^1_\beta|^2 + |\nu^1_\alpha|^2|\nu^1_\beta|^2}{24\pi^2 k_\alpha R^6} + (\alpha \leftrightarrow \beta) \ . \tag{3}$$

In the nonrelativistic limit the matrix elements ν^1_α connecting the ground states with negative energy intermediate states lead to a diamagnetic matrix element, since in this limit:

$$\sum_{\alpha_0\alpha}^{(k_\alpha<0)} k_\alpha^{-1}|\nu^1_\alpha|^2 = -(4m)^{-1}\sum_{\alpha_0}\langle\alpha_0|r^2|\alpha_0\rangle \ . \tag{4}$$

For the dispersive part of $V(R)$, with both atoms in excited intermediate states we get:

$$V_{\mathrm{disp}}(R)=\frac{1}{g_{\mathrm{a}}g_{\mathrm{b}}}\sum_{\alpha_0\beta_0\alpha\beta}{}'' \operatorname{sgn}(E_\alpha)\left\{\boldsymbol{\Gamma}_{\alpha_1}\boldsymbol{\Gamma}_{\beta_1}:(\nabla_1\nabla_1-\mathsf{U}\Delta_1)\boldsymbol{\Gamma}^*_{\alpha_2}\boldsymbol{\Gamma}^*_{\beta_2}:(\nabla_2\nabla_2-\mathsf{U}\Delta_2)\frac{P(|k_\alpha R_1+k_\alpha R_2|)}{8\pi^3(k_\alpha^2-k_\beta^2)k_\alpha^2 k_\beta R_1 R_2}\right.$$
$$\left.-\boldsymbol{\Gamma}_{\alpha_1}\cdot\boldsymbol{\Gamma}_{\beta_1}\,\boldsymbol{\Gamma}^*_{\alpha_2}\cdot\boldsymbol{\Gamma}^*_{\beta_2}\frac{P(|k_\alpha R_1+k_\alpha R_2|)-\frac{1}{2}|k_\alpha R_1+k_\alpha R_2|^{-1}}{8\pi^3 k_\beta R_1 R_2}\right\}+(\alpha\leftrightarrow\beta)\,, \tag{5}$$

with $P(x)$ given in terms of sine and cosine integrals as $\mathrm{ci}(x)\sin x-\mathrm{si}(x)\cos x$. The double prime at the summation sign stands for the conditions $k_\alpha\neq 0$, $k_\beta\neq 0$. In the nonrelativistic limit the expression (5) reduces to that obtained in paper I. At large separations the dominant term of V_{disp} may be written in terms of the electric and magnetic dipole matrix elements in a symmetric way [also ref. 2]:

$$V^{\mathrm{L}}_{\mathrm{disp}}(R)=-\frac{1}{g_{\mathrm{a}}g_{\mathrm{b}}}\sum_{\alpha_0\beta_0\alpha\beta}{}''\frac{23|\mu^1_\alpha|^2|\mu^1_\beta|^2-7|\mu^1_\alpha|^2|\nu^1_\beta|^2-7|\nu^1_\alpha|^2|\mu^1_\beta|^2+23|\nu^1_\alpha|^2|\nu^1_\beta|^2}{144\pi^3 k_\alpha k_\beta R^7} \tag{6}$$

As was the case for the inductive interaction the negative energy intermediate states give rise, in the nonrelativistic limit, to diamagnetic matrix elements. The formula for V_{disp} derived in paper III may be recovered by expressing these diamagnetic matrix elements in electric quadrupole moments with the help of the sum rules given there.

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References

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