The Polarization Model For Valence - Core Correlation In Molecules

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Introduction

The required level of accuracy in calculations of the molecular systems makes that relatively small and subtle effects have to be taken into account. Two important effects are correlation and relativity. Here, we limit ourselves to the electron correlation effects. Practical calculations of systems with heavy atoms are performed with frozen closed-shell cores or replacing these cores by by pseudo-potentials or model potentials. It had been already proved that the so called core-polarization model was very useful. It was used many years ago to improve hand-made Hartree calculations [1]. Recent calculations on atoms have been used to illustrate the importance of correlation effects using the polarization model [2].

The Core - Polarization Model

We assume that the oscillator represents an atomic core and E represents the field from valence electrons. From classical electrodynamic it is well known that the effect of the external field E on the oscillator induces a dipole moment αE and shifts all energy levels by the same amount, $-\frac{1}{2}\alpha E^2$. This enables to model correlation effects by assuming that the core possesses a dipole polarizability α in the presence of the field E.

Interatomic Ineracting At Long Range

We consider two interacting atoms (A and B) at long range. The total hamiltonian can be written as

$$\mathbf{H} = \mathbf{H}_A + \mathbf{H}_B + \mathbf{V}_{AB},$$

where H_A and H_B are the hamiltonians of the isolated atoms and V_{AB} is the interaction between these atoms. A useful approach is given by Baylis [3] provides a practical expression for V_{AB} , where the separate contributions of the valence electrons and the closed-shell cores of atom A and B are considered:

$$\mathbf{V}_{AB} = \mathbf{V}(e_A - e_B) + \mathbf{V}(core_A - core_B) + \mathbf{V}(e_A - core_B) + \mathbf{V}(e_B - core_B),$$

where $V(e_A - e_B)$ is the interaction between the valence electrons of atom A and those of atom B, $V(e_A - core_B)$ is the interaction of the valence electrons of A with the core electrons of B, etc [3].

Self - Core Interaction

The valence self core correlation is given by term

$$-\frac{1}{2}\alpha_A\langle\phi_A|\mathbf{E}_{AA}^2|\phi_A\rangle,$$

where α_A is the static dipole polarizability of the atom A, ϕ_A is the n_A - electron wavefunction and \mathbf{E}_{AA} is the electric field due to all valence electrons and other charged cores, appropriately averaged over the distribution of A. The above term is independent on internuclear separation, so it could be accounted for adjusting of asymptotic energies. In atomic units the electric field at A can be written as

$$\mathbf{E}_{AA} = \sum rac{\mathbf{r_n}}{r_n^3} \chi(r_n),$$

where $\chi(r)$ is the cut-off function. A simple way to extract model polarization parameters is to average the energy adjustment of a given triple state with that of corresponding singlet

$$\frac{1}{2} \left[\langle \phi_A^{(+)} | v + w | \phi_A^{(+)} \rangle + \langle \phi_A^{(-)} | v + w | \phi_A^{(-)} \rangle \right] = \sum_n \langle \psi_n | v_1 | \psi_n \rangle,$$

in which $\phi_A^{(+)}$ and $\phi_A^{(-)}$ are the singlet and triplet wave-functions, respectively, v and w are one- and two-electron (dielectric) terms of the valence-self core interaction $(-\frac{1}{2}\alpha_A\mathbf{E}_{AA}^2\equiv v+w)$, ψ_n is the one electron atomic orbital centered on A. The one-electron term can be written as

$$v = \sum_{n} v_n = -\frac{1}{2} \alpha_A \sum_{n} r_n^{-4} \chi^2(r_n).$$

In fact we have to compare simple average of the energy adjustment for singlet and appropriate triplet to the expression

$$\sum_{n=1}^2 \langle \psi_n^{(e)} | v_1 | \psi_n^{(e)}
angle - \sum_{n=1}^2 \langle \psi_n^{(g)} | v_1 | \psi_n^{(g)}
angle,$$

where $\psi_n^{(e)}$ and $\psi_n^{(g)}$ are the one-electron atomic spin-orbitals of the excited and ground state, respectively, $v_1=-\frac{1}{2}\alpha_A r_1^{-4}\chi^2(r_1)$ is the one-electron term with the cut-off function $\chi(r)$ [4]

$$\chi(r) = \frac{r^3}{(r^2 + r_2^2)^{3/2}}$$

One possibility is to take α_A or r_0 from independent sources. Another values of α_A and r_0 can be find by the least square method.

Other - Core Interaction

Other-core interaction may be represented by the following expression

$$-\frac{1}{2}\alpha_a \mathbf{E}_{AB}^2,$$

where E is the electric field acting on the atom A at D due a positive core charge Z_B of the atom B at the origin and its Z electrons at \mathbf{r}_n , $\{n=1,2\}$. Our aim is to calculate diagonal matrix elements

$$\langle \phi_B | - \frac{1}{2} \alpha_A \mathbf{E}_{AB}^2 | \phi_B \rangle,$$

where ϕ_B is the CI wave-function of the atom B. ϕB is the linear combination of the Slater determinants

$$\phi_B = rac{1}{Z!} \sum_i a_i \cdot det_i(\widetilde{\psi_1}, \widetilde{\psi_2}, \cdots, \widetilde{\psi_Z}).$$

In term every spatial part ψ_k of the spin-orbital $\widetilde{\psi_k}$ is the linear combination of the gaussian type orbitals q_l

$$\psi_k = \sum_l b_l \cdot q_l.$$

In fact the basic elements which have to be calculated are

$$\langle q(1)|v_{AB}|q'(2)\rangle,$$

where v_{AB} is the one-electron other-core interaction operator. To calculate the above matrix elements between two arbitrary gaussians we start with the basic element

$$\langle s(1)|(\mathbf{r}-\mathbf{a}_3)\cdot\widehat{n}\cdot\frac{\chi(|\mathbf{r}-\mathbf{a}_3|)}{|\mathbf{r}-\mathbf{a}_3|^3}|s(2)\rangle.$$

In here

$$\frac{\chi(|\mathbf{r} - \mathbf{a}_3|)}{|\mathbf{r} - \mathbf{a}_3|^3} = \frac{1}{(|\mathbf{r} - \mathbf{a}_3|^2 + r_0^2)^{3/2}} = U^{-3/2} = \frac{1}{\Gamma(\frac{3}{2})} \int_0^\infty \rho'(s) e^{-\alpha_3(\mathbf{r} - \mathbf{a}_3)^2} s^{1/2} ds,$$

where $lpha_3=s$ and $ho'(s)=e^{-sr_0^2}$. Now

$$\langle s(1)|\frac{\chi(|\mathbf{r}-\mathbf{a}_3|)}{|\mathbf{r}-\mathbf{a}_3|^3}|s(2)\rangle = \frac{1}{\Gamma(\frac{3}{2})}\int_0^\infty \rho'(s)Is^{1/2}ds,$$

where ${\cal I}$ is the standard integral. Making further calculations we get

$$\langle s(1)|(\mathbf{r}-\mathbf{a}_3)\cdot\widehat{k}\cdot\frac{\chi(|\mathbf{r}-\mathbf{a}_3|)}{|\mathbf{r}-\mathbf{a}_3|^3}|s(2)\rangle = \frac{1}{2\alpha_3} \frac{\partial}{\partial(\mathbf{a}_3\cdot\widehat{k})}\langle s(1)|\frac{\chi(|\mathbf{r}-\mathbf{a}_3|)}{|\mathbf{r}-\mathbf{a}_3|^3}|s(2)\rangle.$$

All needed elements in the gaussian base are found by use of the above equation, table of integrand factors and bellow equation

$$\frac{1}{2\alpha_3} \quad \frac{\partial}{\partial (\mathbf{a}_3 \cdot \widehat{k})} (\mathbf{r} - \mathbf{a}_2) \cdot \widehat{n} = \frac{\widehat{k} \cdot \widehat{n}}{2A}.$$

Generally

$$\langle q(1)|(\mathbf{r}-\mathbf{a}_3)\cdot\widehat{k}\cdot\frac{\chi(|\mathbf{r}-\mathbf{a}_3|)}{|\mathbf{r}-\mathbf{a}_3|^3}|q'(2)\rangle = \frac{1}{\Gamma(\frac{3}{2})}\int_0^\infty \rho'(s)F'(s)Is^{1/2}ds,$$

where the integrand factor F'(s) is given in Table 1.

Conclusions

We have derived the general expressions for matrix elements of polarization model potential is the gaussian base. Integrand factor has been calculated for differ symmetry of gaussian functions. We are going to apply this approach to Cs_2 diatomic system and next to expand it to cesium cluster.

Integrand Factor F'(s)

q(1)	q'(2)	F '(s)
S	S	$(\mathbf{R} - \mathbf{a}_3) \cdot \widehat{\mathbf{k}}$
s	\mathbf{p}_n	$(\mathbf{R} - \mathbf{a}_3) \cdot \widehat{\mathbf{k}} \cdot (\mathbf{R} - \mathbf{a_2}) \cdot \widehat{\mathbf{n}} + \frac{\widehat{\mathbf{k}} \cdot \widehat{\mathbf{n}}}{2\mathbf{A}}$
\mathbf{p}_m	\mathbf{p}_n	$ \begin{array}{l} (\mathbf{R} - \mathbf{a}_1) \cdot \widehat{\mathbf{m}} \cdot (\mathbf{R} - \mathbf{a}_2) \cdot \widehat{\mathbf{n}} \cdot (\mathbf{R} - \mathbf{a}_3) \cdot \widehat{\mathbf{k}} + \\ + \frac{\widehat{\mathbf{k}} \cdot \widehat{\mathbf{n}}}{2A} (\mathbf{R} - \mathbf{a}_1) \cdot \widehat{\mathbf{m}} + \frac{\widehat{\mathbf{k}} \cdot \widehat{\mathbf{m}}}{2A} (\mathbf{R} - \mathbf{a}_2) \cdot \widehat{\mathbf{n}} + \\ + \frac{\widehat{\mathbf{m}} \cdot \widehat{\mathbf{n}}}{2A} (\mathbf{R} - \mathbf{a}_3) \cdot \widehat{\mathbf{k}} \end{array} $
S	\mathbf{d}_{mn}	$ \begin{array}{l} (\mathbf{R} - \mathbf{a}_2) \cdot \widehat{\mathbf{m}} \cdot (\mathbf{R} - \mathbf{a_2}) \cdot \widehat{\mathbf{n}} \cdot (\mathbf{R} - \mathbf{a_3}) \cdot \widehat{\mathbf{k}} + \\ + \frac{\widehat{\mathbf{k}} \cdot \widehat{\mathbf{m}}}{2A} (\mathbf{R} - \mathbf{a}_2) \cdot \widehat{\mathbf{n}} + \frac{\widehat{\mathbf{k}} \cdot \widehat{\mathbf{n}}}{2A} (\mathbf{R} - \mathbf{a_2}) \cdot \widehat{\mathbf{m}} + \\ + \frac{\widehat{\mathbf{m}} \cdot \widehat{\mathbf{n}}}{2A} (\mathbf{R} - \mathbf{a_3}) \cdot \widehat{\mathbf{k}} \end{array} $
\mathbf{p}_l	\mathbf{d}_{mn}	$ \begin{array}{l} (\mathbf{R} \boldsymbol{\cdot} \mathbf{a}_1) \cdot \widehat{\mathbf{l}} \cdot (\mathbf{R} - \mathbf{a}_2) \cdot \widehat{\mathbf{m}} \cdot (\mathbf{R} - \mathbf{a}_2) \cdot \widehat{\mathbf{n}} \cdot (\mathbf{R} - \mathbf{a}_3) \cdot \widehat{\mathbf{k}} + \\ + \frac{\widehat{\mathbf{m}} \cdot \widehat{\mathbf{n}}}{2A} \left(\mathbf{R} \boldsymbol{\cdot} \mathbf{a}_1 \right) \cdot \widehat{\mathbf{l}} \cdot (\mathbf{R} - \mathbf{a}_3) \cdot \widehat{\mathbf{k}} + \frac{\widehat{\mathbf{l}} \cdot \widehat{\mathbf{m}}}{2A} (\mathbf{R} - \mathbf{a}_2) \cdot \widehat{\mathbf{n}} \cdot \\ \cdot (\mathbf{R} - \mathbf{a}_3) \cdot \widehat{\mathbf{k}} + \frac{\widehat{\mathbf{l}} \cdot \widehat{\mathbf{n}}}{2A} (\mathbf{R} - \mathbf{a}_2) \cdot \widehat{\mathbf{m}} \cdot (\mathbf{R} - \mathbf{a}_3) \cdot \widehat{\mathbf{k}} + \\ + \frac{\widehat{\mathbf{k}} \cdot \widehat{\mathbf{l}}}{2A} \left(\mathbf{R} \boldsymbol{\cdot} \mathbf{a}_2 \right) \cdot \widehat{\mathbf{m}} \cdot (\mathbf{R} - \mathbf{a}_2) \cdot \widehat{\mathbf{n}} + \frac{\widehat{\mathbf{k}} \cdot \widehat{\mathbf{m}}}{2A} (\mathbf{R} - \mathbf{a}_1) \cdot \widehat{\mathbf{l}} \cdot \\ \cdot (\mathbf{R} - \mathbf{a}_2) \cdot \widehat{\mathbf{n}} + \frac{\widehat{\mathbf{k}} \cdot \widehat{\mathbf{n}}}{2A} (\mathbf{R} - \mathbf{a}_1) \cdot \widehat{\mathbf{l}} \cdot (\mathbf{R} - \mathbf{a}_2) \cdot \widehat{\mathbf{m}} + \\ + (\frac{1}{2A})^2 \left(\widehat{\mathbf{m}} \cdot \widehat{\mathbf{n}} \cdot \widehat{\mathbf{k}} \cdot \widehat{\mathbf{l}} + \widehat{\mathbf{l}} \cdot \widehat{\mathbf{m}} \cdot \widehat{\mathbf{k}} \cdot \widehat{\mathbf{n}} + \widehat{\mathbf{l}} \cdot \widehat{\mathbf{n}} \cdot \widehat{\mathbf{k}} \cdot \widehat{\mathbf{m}} \right) \end{array} $
\mathbf{d}_{hl}	\mathbf{d}_{mn}	$\begin{array}{l} (R - a_1) \cdot \widehat{h} \cdot (R - a_1) \cdot \widehat{l} \cdot (R - a_2) \cdot \widehat{m} \cdot (R - a_2) \cdot \widehat{n} \cdot \\ \cdot (R - a_3) \cdot \widehat{k} + \frac{\widehat{m} \cdot \widehat{n}}{2A} (R - a_1) \cdot \widehat{h} \cdot (R - a_1) \cdot \widehat{l} \cdot \\ \cdot (R - a_3) \cdot \widehat{k} + \frac{\widehat{m} \cdot \widehat{n}}{2A} (R - a_2) \cdot \widehat{m} \cdot (R - a_2) \cdot \widehat{n} \cdot \\ \cdot (R - a_3) \cdot \widehat{k} + \frac{\widehat{l} \cdot \widehat{n}}{2A} (R - a_1) \cdot \widehat{h} \cdot (R - a_2) \cdot \widehat{m} \cdot \\ \cdot (R - a_3) \cdot \widehat{k} + \frac{\widehat{l} \cdot \widehat{n}}{2A} (R - a_1) \cdot \widehat{h} \cdot (R - a_2) \cdot \widehat{m} \cdot \\ \cdot (R - a_3) \cdot \widehat{k} + \frac{\widehat{h} \cdot \widehat{n}}{2A} (R - a_1) \cdot \widehat{l} \cdot (R - a_2) \cdot \widehat{m} \cdot \\ \cdot (R - a_3) \cdot \widehat{k} + \frac{\widehat{h} \cdot \widehat{m}}{2A} (R - a_1) \cdot \widehat{l} \cdot (R - a_2) \cdot \widehat{m} \cdot \\ \cdot (R - a_3) \cdot \widehat{k} + (\frac{1}{2A})^2 (\widehat{h} \cdot \widehat{l} \cdot \widehat{m} \cdot \widehat{n} + \widehat{h} \cdot \widehat{m} \cdot \widehat{l} \cdot \widehat{n} + \widehat{h} \cdot \widehat{n} \cdot \widehat{l} \cdot \widehat{m}) \cdot \\ \cdot (R - a_3) \cdot \widehat{k} + \frac{\widehat{k} \cdot \widehat{n}}{2A} (R - a_1) \cdot \widehat{l} \cdot (R - a_2) \cdot \widehat{m} \cdot \\ \cdot (R - a_3) \cdot \widehat{k} + \frac{\widehat{k} \cdot \widehat{n}}{2A} (R - a_1) \cdot \widehat{l} \cdot (R - a_2) \cdot \widehat{m} \cdot \\ \cdot (R - a_2) \cdot \widehat{n} + \frac{\widehat{k} \cdot \widehat{n}}{2A} (R - a_1) \cdot \widehat{h} \cdot (R - a_2) \cdot \widehat{m} \cdot \\ \cdot (R - a_2) \cdot \widehat{n} + \frac{\widehat{k} \cdot \widehat{m}}{2A} (R - a_1) \cdot \widehat{h} \cdot (R - a_2) \cdot \widehat{n} \cdot \\ \cdot (R - a_2) \cdot \widehat{m} + \frac{\widehat{k} \cdot \widehat{n}}{2A} (R - a_1) \cdot \widehat{h} \cdot (R - a_2) \cdot \widehat{l} \cdot \\ \cdot (R - a_2) \cdot \widehat{m} + \frac{\widehat{m} \cdot \widehat{n} \cdot \widehat{k} \cdot \widehat{h}}{(2A)^2} (R - a_1) \cdot \widehat{l} + \frac{\widehat{m} \cdot \widehat{n} \cdot \widehat{k} \cdot \widehat{k}}{(2A)^2} (R - a_2) \cdot \widehat{m} + \\ + \frac{\widehat{h} \cdot \widehat{n} \cdot \widehat{k} \cdot \widehat{n}}{(2A)^2} (R - a_2) \cdot \widehat{m} + \frac{\widehat{h} \cdot \widehat{n} \cdot \widehat{k} \cdot \widehat{n}}{(2A)^2} (R - a_1) \cdot \widehat{h} + \\ + \frac{\widehat{h} \cdot \widehat{m} \cdot \widehat{k} \cdot \widehat{l}}{(2A)^2} (R - a_2) \cdot \widehat{m} + \frac{\widehat{h} \cdot \widehat{m} \cdot \widehat{k} \cdot \widehat{m}}{(2A)^2} (R - a_1) \cdot \widehat{l} + \\ + \frac{\widehat{h} \cdot \widehat{m} \cdot \widehat{k} \cdot \widehat{l}}{(2A)^2} (R - a_2) \cdot \widehat{m} + \frac{\widehat{h} \cdot \widehat{m} \cdot \widehat{k} \cdot \widehat{m}}{(2A)^2} (R - a_1) \cdot \widehat{l} + \\ + \frac{\widehat{h} \cdot \widehat{m} \cdot \widehat{k} \cdot \widehat{l}}{(2A)^2} (R - a_2) \cdot \widehat{m} + \frac{\widehat{h} \cdot \widehat{m} \cdot \widehat{k} \cdot \widehat{m}}{(2A)^2} (R - a_1) \cdot \widehat{l} + \\ + \frac{\widehat{h} \cdot \widehat{m} \cdot \widehat{k} \cdot \widehat{l}}{(2A)^2} (R - a_2) \cdot \widehat{m} + \frac{\widehat{h} \cdot \widehat{m} \cdot \widehat{k} \cdot \widehat{m}}{(2A)^2} (R - a_1) \cdot \widehat{l} + \\ + \frac{\widehat{h} \cdot \widehat{m} \cdot \widehat{k} \cdot \widehat{l}}{(2A)^2} (R - a_2) \cdot \widehat{m} + \frac{\widehat{h} \cdot \widehat{m} \cdot \widehat{k} \cdot \widehat{m}}{(2A)^2} (R - a_1) \cdot \widehat{l} + \\ + \frac{\widehat{h} \cdot \widehat{m} \cdot \widehat{k} \cdot \widehat{l}}{(2A)^2} (R - a_2) \cdot \widehat{m} + \frac{\widehat{h} \cdot \widehat{m} \cdot \widehat{k} \cdot \widehat{m}}{(2A)^2} (R - a_1) \cdot \widehat{l} + \\ + \frac{\widehat{h} \cdot \widehat$

TABLE 1. Integrand factor F'(s).

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