Hartree-Fock Calculations of the Interaction Potential Parameters for Noble-Gas Atoms

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The interaction potential parameters ($\langle r^k \rangle$, Hindmarsh's radius r_H , C_6 , C_8 , C_{12}) are calculated for the ground and some excited configurations of the noble-gas atoms from the Hartree-Fock functions. A formula for the C_8 constant is derived.

1. Introduction

The phenomenon of the pressure broadening of spectral lines is actually the main source of information about interactions between the ground- and excited-state atoms in the gas phase. In the last few years the quantum theory of the pressure line broadening has been widely developed. However, in order to compare the results of these theories with experiment the detailed knowledge of the interaction potential between the emitter (excited-state atom) and the perturber (ground-state atom) is necessary. These potentials are precisely known in only very few cases. Therefore different approximate formulae, such as the model function of the Lennard-Jones type, are rather frequently applied. These model potentials were shown to be very important in many applications of the line broadening studies, first of all in astrophysics and plasma diagnostics (cf. e.g. [4]).

In this paper we present the results of Hartree-Fock calculations of some basic atomic parameters, appearing in these approximate formulae. These parameters can be used to estimate the interaction energies of the ground-state noble-gas atoms with other atoms. In the case of neon atom we present also the corresponding parameters for excited configurations, because the pressure broadening of the neon spectral lines is studied experimentally in our laboratory. In this case an estimate of the C_6 , C_8 and C_{12} constants for the interaction of excited neon with the ground-state neon and helium atoms

was also possible. Despite recent progress in the interaction-constant calculations (cf. e.g. [8]) it seems, that some simple methods of their estimation, particularly for the excited states, are still of value for experimentalists. Our own derivation of the C_8 interaction constant is also presented.

2. Interaction Energy

The first two terms in the hamiltonian of two atoms interacting at long distance, in the molecule-oriented coordinate system (z -axis along the line emitter-perturber) have the form [1]:

$$\begin{aligned} V(R_p, \mathbf{r}) \equiv H' + H'' \\ = (e^2/R_p^3)(xx_p + yy_p - 2zz_p) \\ + \frac{3}{2}(e^2/R_p^4) \\ \cdot (r_p^2 - zr_p^2 + 2xx_p \\ + 2yy_p - 3z^2z_p \\ - 2xx_pz_p - 2yy_pz_p \\ + 3zz_p^2). \end{aligned} \quad (1)$$

Here, R_p is the interatomic (emitter-perturber) distance, the unsubscripted coordinates measure the electronic position relative to the emitter nucleus, the p -subscripted ones its position relative to the perturber nucleus.

Within the second-order perturbation theory the first of these two terms gives us the well-known Van-der-Waals potential, $-C_6 R_p^{-6}$. Assuming the perturber atom, e.g. the noble-gas one, in the $1S_0$ ground state, and the $|KJM\rangle$ state of the emitter (K represents the set of other quantum numbers necessary), the C_6 interaction constant can be expressed as, cf. [2, 3]:

$$\begin{aligned} C_6(KJM) = \frac{\sigma_p I_p}{2(2J+1)} \\ \cdot \sum_{K'J'} \frac{S(KJ, K'J')[1 + 3(1J'0M|JM)^2]}{E_{K'J'} - E_{KJ} + I_p}. \end{aligned} \quad (2)$$

In this formula the summation runs over all the states $|K'J'\rangle$ of the emitter, $E_{KJ}, E_{K'J'}$ are the corresponding state energies and $S(KJ, K'J')$ the dipole line strengths. Other quantities concern the perturber atom: σ_p is its dipole polarizability, I_p — the ionization potential; $(1J'0M|JM)$ is the Clebsch-Gordan coefficient.

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On the same level of approximation, assuming still the $1S_0$ state for the perturber, one obtains from the second part of (1) the $-C_8 R_p^{-8}$ term of the long-range potential, with the force constant given by

$$C_8(KJM; K_p J_p) = \frac{9}{4} e^2 \sum_{K'J'M'} \sum_{K_p'J_p'} \frac{1}{E_{K'J'} - E_{KJ} + E_{K_p'J_p'} - E_{K_p J_p}} \cdot \{ \frac{1}{3} S_{(d)}(K_p J_p, K_p' J_p') [|\langle KJM | r^2 | K'J'M' \rangle|^2 + 9 |\langle KJM | z^2 | K'J'M' \rangle|^2 + 4 |\langle KJM | xz | K'J'M' \rangle|^2 + 4 |\langle KJM | yz | K'J'M' \rangle|^2] + \frac{2}{3} S_{(q)}(K_p J_p, K_p' J_p') [|\langle KJM | x | K'J'M' \rangle|^2 + |\langle KJM | y | K'J'M' \rangle|^2 + 3 |\langle KJM | z | K'J'M' \rangle|^2] \}. \quad (3)$$

Here, the second sum concerns the $|K_p' J_p'\rangle$ states of the perturber, $E_{K_p J_p}, E_{K_p' J_p'}$ are the corresponding perturber state energies and $S_{(d)}, S_{(q)}$ are the line strengths for, respectively, the dipole and quadrupole transitions in the perturber atom. After application of the Wigner-Eckart theorem, taking into consideration the definition of polarizabilities and assuming (as in the case of the C_6 expression) that the energy differences $E_{K_p' J_p'} - E_{K_p J_p}$ are approximately equal to the ionization potential I_p of the perturber, we obtain the following approximate formula:

$$C_8(KJM) = \frac{9}{4} \frac{I_p}{(2J+1)} \sum_{K'J'} \frac{1}{E_{K'J'} - E_{KJ} + I_p} \cdot \{ \sigma_p S_{(q)}(KJ, K'J') [3(2J'OM|JM)^2 + (2J'-1M+1|JM)^2 + (2J'1M-1|JM)^2] + \frac{3}{5} \sigma_{p(q)} S(KJ, K'J') [1 + 2(1J'OM|JM)^2] \}. \quad (4)$$

where $S_{(q)}(KJ, K'J')$ is the line strengths for the quadrupole transitions in the emitter, $\sigma_{p(q)}$ is the quadrupole polarizability of the perturber, all the other quantities have been discussed previously.

It is rather difficult to use the above written formulae (2, 4) for calculations of the C_6 and C_8 interaction constants, because one should know the line strengths $S(KJ, K'J')$, $S_{(q)}(KJ, K'J')$ for all the lines corresponding to the transitions from the $|KJ\rangle$ state of the emitter. For this reason some more approximate formulae are in common use. The C_6 constant can be calculated in the Unsöld approximation [4] as

$$C_6 = e^2 \sigma_p \langle r^2 \rangle. \quad (5)$$

For the C_8 constant the approximate formula of Davison [5] is known:

$$C_8 = \frac{3}{2} e^2 \sigma_p \langle r^4 \rangle + \frac{5}{2} e^2 \sigma_{p(q)} \langle r^2 \rangle. \quad (6)$$

In these expressions $\langle r^k \rangle$ means the average value of the corresponding power of the optical electron radial coordinate (relative to the emitter nucleus).

The Van-der-Waals interaction energy,

$$\Delta E(R_p) = -C_6 R_p^{-6} - C_8 R_p^{-8} \quad (7)$$

includes only the attractive forces. In many cases the pressure line broadening can be correctly described using only the first term of (7). However in some cases (e.g. when the helium atom is used as the perturber) the inclusion of repulsive forces becomes necessary. The simplest way to do this is the application of the Lennard-Jones potential

$$\Delta E(R_p) = C_{12} R_p^{-12} - C_6 R_p^{-6}, \quad \text{or} \\ \Delta E(R_p) = C_{12} R_p^{-12} - C_6 R_p^{-6} - C_8 R_p^{-8}. \quad (8)$$

Hindmarsh et al. [6] gave an empirical method of estimation of the C_{12} constant. According to these authors

$$C_{12} = q (r_H + r_{H_p})^{12}, \quad (9)$$

where q is an empirical constant and r_H, r_{H_p} are the "Hindmarsh's radii" of emitter and perturber, respectively. These Hindmarsh's radii can be easily extracted from the long-distance shape of the radial electron density, as described in [6].

3. Numerical Calculations and Discussion

For the calculations of the expectation values $\langle r^2 \rangle, \langle r^4 \rangle$ (5, 6) and the Hindmarsh's radii r_H (9) we have used the numerical Hartree-Fock orbitals. The Hartree-Fock equations for the ground states of the noble-gas atoms, He to Xe, and for some excited configurations of the neon atom have been

Units: ^a atomic units; ^b 10^{-58} erg cm⁶; ^c 10^{-71} erg cm⁸; ^d erg cm¹².

Ne*-Ne and Ne*-He interactions the potential parameters presented here have recently been used (Refs. [12–15]) for calculations of the pressure broadening coefficients for the neon spectral lines arising from the transitions between the levels belonging to configurations: $2p^53s$ - $2p^53p$; $2p^53p$ - $2p^54d$; $2p^53p$ - $2p^55s$, studied experimentally in our laboratory. A reasonable agreement between the calculated and experimental coefficients has been noted. This indicates that within the approximation level represented by the formulae (5, 6, 9) the electron correlation effects are of lower importance and the Hartree-Fock approxi-

mation alone can be effectively used for interpretation of the pressure line broadening experiments.

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- [1] H. Margenau, *Phys. Rev.* **40**, 382 (1932), *Rev. Mod. Phys.* **11**, 1 (1939).
- [2] J. Fiutak and M. Frackowiak, *Bull. Acad. Polon. Sci. Ser. Sci. Math. Astr. Phys.* **11**, 175 (1963).
- [3] A. Bielski and J. Szudy, *Z. Naturforsch.* **30a**, 1903 (1975).
- [4] A. Unsold, *Physik der Sternatmosphären*, Springer Verlag, Berlin 1955.
- [5] W. D. Davison, *J. Phys. B*, **1**, 139 (1968).
- [6] W. R. Hindmarsh, A. D. Petford, and B. Smith, *Proc. Roy. Soc. London A* **297**, 296 (1967).
- [7] C. Froese Fischer, *The Hartree-Fock Method for Atoms: A Numerical Approach*, Wiley-Intersci. New York 1977.
- [8] F. Maeder and W. Kutzelnigg, *Chem. Phys.* **42**, 95 (1979).
- [9] W. R. Hindmarsh and J. M. Farr, *Collision Broadening of Spectral Lines by Neutral Atoms*, in *Progress in Quantum Electronics*, Vol. 2, Part 3, edited by J. M. Sanders and S. Stenholm, Pergamon Press, London 1972.
- [10] Landolt-Börnstein, *Atom und Molekularphysik*, Vol. 1, 1950, p. 401.
- [11] A. Dalgarno, *Adv. Phys.* **11**, 281 (1962).
- [12] A. Bielski and J. Wolnikowski, *Acta Phys. Polon.* **A54**, 601 (1978).
- [13] A. Bielski, E. Lisicki, M. Nesterov, and J. Wolnikowski, *Acta Phys. Polon.* **A54**, 611 (1978).
- [14] A. Bielski, S. Birza, K. Bystra, and W. Dokurno, *Physika* **97C**, 249 (1979).
- [15] A. Bielski, W. Dokurno, J. Szudy, and J. Wolnikowski, *Physica* **101 C**, 113 (1980).