# Interatomic Potentials and applications to Spectral Line Broadening

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- Interatomic Potentials; their Modelling and Accuracy
- Spectral Line Broadening; Validity of Van der Waals Formula

## Interatomic Potentials

• Large quantum chemistry calculations provide very accurate potentials for electronic states of atom-atom systems at short and intermediate separations.

Limited to low excited electronic states.

• Present problems involve low-energy scattering processes for excited electronic states.

Requirement: Accurate representation of potentials at medium and large interatomic separations.

## Modelling of atom-atom system

• Three-body model: two atomic cores and one active electron, i.e. $A^{m+} + B^{n+} + e^-$.

Examples: $Na^+ + H + e^-$; $Na^{2+} + H^+ + e^-$.

• Electron-core interaction.

$$V_{a,b}(r) = -\frac{Z}{r}(1 + \delta + \delta' r)\exp(-\alpha r)$$
$$-\frac{z}{r} - \frac{\alpha_d}{2r^4} F_1(r) - \frac{\alpha_q - 6\beta_d}{2r^6} F_2(r)$$
$$+ small\ energy\ term\ (optional)\ ,$$

where $Z + z$=nuclear charge, $z = m, n$ and $F_1(r)$ and $F_2(r)$ are cutoff factors.
Parameters $\alpha$, $\delta$ and $\delta'$ are varied to reproduce the positions of known energy levels for $z \neq 0$, and phase shifts for scattering for $z = 0$. The fits also predict the correct number of nodes in the wave functions.

- Core-core interaction.

$$V_c(R) \simeq -z_a^2 \frac{\alpha_d^b}{2R^4} - z_b^2 \frac{\alpha_q^a}{2R^6}$$

$$+\text{short} - \text{range terms}.$$

Options for short-range term.

(a) Use the three-body model itself to generate potential.
(b) Use simple analytic form based on perturbation theory.

Choices (a) and (b) differ only for $R \leq R_A + R_B$ where $R_A$ and $R_B$ are the mean radii of the cores $A^{m+}$ and $B^{n+}$.

- Three-body interaction.

$$V_3(\mathbf{r},\mathbf{R}) \simeq \frac{\alpha_d}{r^2R^2}\,P_1(\hat{r}\cdot\hat{R}) + \frac{\alpha_q}{r^3R^3}\,P_2(\hat{r}\cdot\hat{R})$$
$$+ \textit{small energy term (optional)}\,,$$

for $R$ large, where $R$ is the internuclear separation. $P_1(\hat{r}\cdot\hat{R})$ and $P_2(\hat{r}\cdot\hat{R})$ are Legendre polynomials.

- The model Hamiltonian.

$$H = -\frac{1}{2}\nabla^2 + V_a(r_a) + V_b(r_b) + V_c(R)$$
$$+ V_3(\mathbf{r_a},\mathbf{R}) + V_3(\mathbf{r_b},\mathbf{R})$$

where $r_a$ and $r_b$ are the position vectors of the electron relative to cores $A$ and $B$. A set of atomic basis states on one or both centres is used and the Hamiltonian matrix diagonalized to obtain the electronic energies.

## Principles and Problems

(a) The long-range interactions are based on well-known perturbation theory.
(b) No existing data for the molecule is used to fix any variable parameters.

(c) Positions of virtual states in electron-core model potentials are sensitive to precise fit.
(d) Model potentials can be l-dependent or l-independent.
(e) A different potential may have to be used for ground states, e.g. He($1s^2$).

## Potential calculations in progress

• Extensive tests are being carried out on the Na*–H system. Quantum chemistry calculations exist for some electronic states which are being used to assess the accuracy of the present calculations at short range.

T. Leininger, F.X. Gadéa and A.S. Dickinson, $J.Phys.B : At.Mol.Opt.Phys.$ **33**, 1805-17 (2000); R.E. Olson and B. Liu, $J.Chem.Phys.$ **73**, 2817-24 (1980).

There is much less information available for the Ne*–Ne and Ar*–Ar systems and within the current model there is no allowance for the homonuclear symmetry. Input data for the three-body model is ready, but awaits the completion of the Na*-H investigation.

## Spectral Line Broadening

• Lindholm Impact Theory. The collision is treated semi-classically. The half-half width $w$ and shift $d$ are given by

$$w + \mathrm{i}d = 2\pi N\{\int v f(v)\mathrm{d}v \int_0^\infty [1 - \exp(\mathrm{i}\eta)]\rho\mathrm{d}\rho\}_{Av}.$$

where *'Av'* denotes an average over degenerate components of the line and $f(v)$ is the Maxwell distribution. The phase shift $\eta$ is obtained from

$$\eta(\rho, v) = -\frac{1}{\hbar}\int_{-\infty}^{\infty} V(t)\,\mathrm{d}t$$

For Van der Waals broadening $V(t)$ is replaced by $-C_6/R^6(t)$, a straight-line path for the relative motion is assumed and the integrals can be evaluated analytically.

G. Peach, *Adv. Phys.* **30**, 367-474 (1981).

• Quantum mechanical Impact Theory. We make the transition

$$(Mv\rho)^2 \rightarrow \hbar^2\, l(l+1).$$

Then

$$2\rho \mathrm{d}\rho \rightarrow \frac{\hbar^2}{(Mv)^2}\,(2l+1)\Delta l\,,$$

the integral over $\rho$ is replaced by a sum over $l$ and

$$\eta(\rho, v) \rightarrow 2\,[\eta_i(l, v) - \eta_f(l, v)]\,,$$

where $\eta_i(l, v)$ and $\eta_f(l, v)$ are elastic scattering phase shifts.

• Born Impact theory. Born approximation is used for $\eta_i$ and $\eta_f$, i.e. plane waves for the scattering wave functions plus first-order perturbation theory.

G. Peach and I.B. Whittingham, SCSLSA7, *New Astronomy Reviews*, in press (2009).

Transition Li $2p^2P$–$2s^2S$ at 670.97 nm.

Half half-widths $w/N$ (in units of $10^{-21}$MHz $m^3$/atom $= (2\pi)^{-1} \times 10^{-9}$rad $s^{-1}$ $cm^3$/atom)

| $T$(K) | Impact Theory | Born Impact Theory | Van der Waals Theory |
|---|---|---|---|
| 70.0 | 0.1476 | 0.1015 | 0.0847 |
| 80.0 | 0.1546 | 0.1074 | 0.0882 |
| 100.0 | 0.1674 | 0.1180 | 0.0943 |
| 200.0 | 0.2184 | 0.1584 | 0.1161 |
| 300.0 | 0.2567 | 0.1883 | 0.1311 |
| 500.0 | 0.3147 | 0.2342 | 0.1528 |
| 700.0 | 0.3599 | 0.2702 | 0.1690 |
| 1000.0 | 0.4151 | 0.3145 | 0.1881 |
| 1500.0 | 0.4882 | 0.3734 | 0.2124 |
| 2000.0 | 0.5477 | 0.4217 | 0.2316 |
| 2500.0 | 0.5985 | 0.4634 | 0.2476 |
| 3000.0 | 0.6433 | 0.5004 | 0.2615 |

Transition Na $3p^2P$–$3s^2S$ at 589.36 nm.

Half half-widths $w/N$ (in units of $10^{-21}$MHz $m^3$/atom $= (2\pi)^{-1} \times 10^{-9}$rad $s^{-1}$ $cm^3$/atom)

| $T$(K) | Impact Theory | Born Impact Theory | Van der Waals Theory |
|---|---|---|---|
| 70.0 | 0.1504 | 0.1174 | 0.1097 |
| 80.0 | 0.1590 | 0.1242 | 0.1142 |
| 100.0 | 0.1745 | 0.1367 | 0.1221 |
| 200.0 | 0.2312 | 0.1839 | 0.1504 |
| 300.0 | 0.2714 | 0.2188 | 0.1698 |
| 500.0 | 0.3320 | 0.2723 | 0.1979 |
| 700.0 | 0.3793 | 0.3144 | 0.2190 |
| 1000.0 | 0.4374 | 0.3662 | 0.2437 |
| 1500.0 | 0.5149 | 0.4354 | 0.2752 |
| 2000.0 | 0.5779 | 0.4922 | 0.3000 |
| 2500.0 | 0.6319 | 0.5411 | 0.3208 |
| 3000.0 | 0.6795 | 0.5846 | 0.3388 |

## Transition Na $3d^2D$–$3p^2P$ at 819.32 nm.

Half half-widths $w/N$ (in units of $10^{-21}$MHz $m^3$/atom $= (2\pi)^{-1} \times 10^{-9}$rad $s^{-1}$ $cm^3$/atom)

| $T$(K) | Impact Theory | Van der Waals Theory |
|---|---|---|
| 70.0 | 0.2505 | 0.2035 |
| 80.0 | 0.2642 | 0.2118 |
| 100.0 | 0.2891 | 0.2265 |
| 200.0 | 0.3853 | 0.2789 |
| 300.0 | 0.4559 | 0.3149 |
| 500.0 | 0.5607 | 0.2671 |
| 700.0 | 0.6411 | 0.4061 |
| 1000.0 | 0.7384 | 0.4519 |
| 1500.0 | 0.8649 | 0.5104 |
| 2000.0 | 0.9639 | 0.5564 |
| 2500.0 | 1.0450 | 0.5949 |
| 3000.0 | 1.1137 | 0.6284 |