

Intermolecular interactions and molecular spectroscopy: from the semiclassical representation of quantum theory to the line wing theory

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The formulation of concepts of classical and quantum potentials within the semiclassical representation is given, their role in the line wing theory is described, the classic character of the intermolecular interaction potential appearing in thermodynamic coefficients is shown. The temperature dependence of the absorption coefficient in the CO₂ and H₂O line wings and the temperature behavior of the second virial coefficients of these gases are discussed.

1. Method of semiclassical representation

Method of semiclassical representation¹ is effective for problems of a definite type. There are two interacting subsystems (and the interaction can not be ignored): essentially quantum and classical. This can be exemplified by the problem on collisional line profile in a gas spectrum (see details in Ref. 2). The first subsystem here is intramolecular degrees of freedom of interacting molecules and the second one is their centers of mass.

It is easier to explain an idea of the method assuming that the problem of contour is already reduced to the binary variant. An exact Hamiltonian in this case is

$$H = H_1(x) + H_2(y) + K(q) + U(x, y, q), \quad (1)$$

where $H_1(x)$ is the Hamiltonian of quantum degrees of freedom of x , directly interacting with the molecule field; $H_2(y)$ is the same for a "buffer" molecule; $K(q)$ is the operator of kinetic energy of the centers of mass q ; U is the Coulomb potential of the intermolecular interaction. The evolution operator is presented as

$$S = BCQ. \quad (2)$$

Here C designates the evolution operator for the Hamiltonian

$$H = H_1(x) + H_2(y) + U(x, y, q), \quad (3)$$

which determines the deformation of quantum states of the molecules, centers of mass of which follow the (multidimensional) classical trajectory $q(t)$, where t is the time. Hamiltonian of an equation for $B(q)$ is constructed so that corresponding matrix elements

are calculated via the solution of classical problem with the potential V , which should regulate the dynamics of centers of mass. The operator Q corrects such separation of variables. Pragmatic efficiency of the method is to be secured by the closeness of $\|Q\|$ to unit. This absolutely natural fact leads to the problem of the corresponding rational choice of $V(q)$, which turns out to be correlated with the quantum mean U by the Gibbs statistical matrix R with the Hamiltonian H and, hence, the parameters of V turn out to be dependent on the temperature Θ .

It is already evident, that two characteristics of an intermolecular interaction are to appear in the problem of two interacting subsystems with Hamiltonian (1), i.e., the quantum potential U at $q \rightarrow q(t)$ and the classical potential V . The sense of these terms is clear from interpreting the multipliers in Eq. (2).

One more essential element of the method is the possibility to transfer the Q problem to statistical part of the task, varying the statistical matrix in standard way when calculating quantum means, finally resulting in the equation for the statistical matrix in classical limit for the dynamics of centers of mass:

$$\rho = \rho_1 \rho_2 G, \quad (4)$$

where ρ_1 and ρ_2 are the Gibbs statistical matrices for $H_1(x)$ and $H_2(y)$; G is the Boltzmann multiplier with the potential V .

2. Second virial coefficient and line profile in wing

Direct calculation of the classical potential V is a complicated problem, but there is a workaround, based on a correlation of the classical potential with thermodynamic gas parameters (virial coefficients,

constants of transfer processes description, etc.). Participation of the classical potential in equations for thermodynamic parameters is the direct consequence of applying the method of semiclassical representation to corresponding equations of statistical physics.

The virial coefficient expressed via V immediately follows statistical sum calculating by Eq. (4). Transfer constants are calculated via quantum means of the operators dependent only on q , and further application of Eq. (2) leaves the only dependence on V (after mention the Liouville theorem).

Asymptotic assessment of the quantum correlation function of dipole moment along with the method of semiclassical representation allow the periphery of spectral line profile to be described in the form²

$$\kappa(\omega) \sim D \frac{1}{\tilde{r}} \int_0^{r_s} \frac{e^{-V(r)/kT}}{\sqrt{\tilde{r}^2 - r^2}} r dr \quad (5)$$

with an accuracy to known multiplier $\kappa(\omega)$ being the ω -radiation absorption coefficient of ω_0 -centered spectral line; $\tilde{r}(\omega, \omega_0)$ is the root of equation $E'' - E' = \hbar\omega$, where E'' and E' are the eigenvalues of Hamiltonian (3), corresponding to the spectral line (\hbar is the Planck constant). As it follows from the definition, an explicit view of Eq. (5) determines the quantum potential. When V is considered as central (k is the Boltzmann constant), $q \rightarrow r$ is the distance between molecules; D depends (in a sufficiently complicated way) on all the Hamiltonians participating in the problem. An applicability condition of Eq. (5) is $|\omega - \omega_0| \gg \gamma$, where γ is the line halfwidth.

Calculation of D and \tilde{r} supposes preliminary solution of the Lippmann–Schwinger equation with all quantum details, which is hardly possible with an acceptable spectroscopic accuracy. Therefore, Equation (5) is interpreted as an approximation equation, allowing classical and quantum potentials to be restored from experimental values of absorption coefficients. Details of the solution of the corresponding inverse problem are thoroughly discussed (and illustrated) in Refs. 2–4 (and their references).

The above facts give a possibility to compare values obtained in independent experiments, i.e., the classical potential of intermolecular interaction, determined from the temperature dependence of the second virial coefficient, and spectral data on absorption coefficients at different temperatures. The quantum potential U in the last case is considered as temperature independent. In addition, the integral multiplier in Eq. (5) essentially determines the dependence of absorption coefficient on the temperature and pressure.

3. 4.3 μm band of CO_2

The classical potential V for CO_2 molecule at a standard temperature was approximated by the Lennard–Jones potential with parameters, thermodynamically measured at this temperature.⁵ Parameters of the quantum potential at a given classical potential was

recovered in Refs. 2–4 from the measured^{6,7} absorption coefficient in a wing of the 4.3 μm band. The quantum coefficient was further considered as invariable; parameters of the classical potential were found from experimental values of absorption coefficients at other temperatures, thus being temperature dependent. Further, using the classical potential obtained from the analysis of absorption coefficient in line wings, the second virial coefficient was calculated:

$$B(T) = -\frac{2\pi N_0}{3kT} \int_0^\infty e^{-V(R)/kT} \frac{dV(R)}{dR} R^3 dR. \quad (6)$$

The obtained temperature dependence of the virial coefficient is shown in Fig. 1 together with experimental data on this parameter. Figure 2 shows the quantum potential.

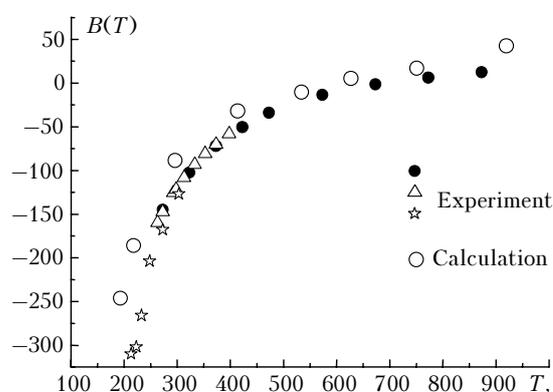


Fig. 1. The second virial coefficient, calculated with the classical potential of intermolecular interaction, obtained from the data on CO_2 absorption coefficient in the 4.3 μm band, in comparison with the experimental^{12–14} data.

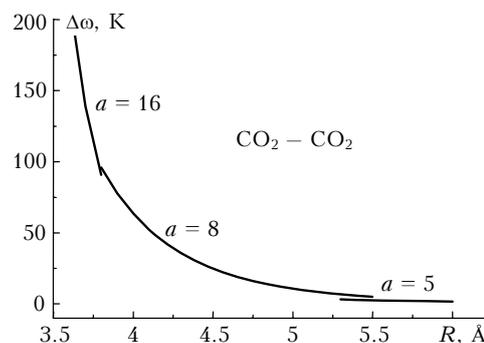


Fig. 2. Approximations of the quantum potential of interaction $\Delta E \sim \Delta\omega = (C/R)^a$, used in calculation of CO_2 absorption coefficient near 4.3 μm .

4. 8–12 μm range in the water vapor spectrum

Available potentials, tested in Ref. 8, did not give a good description of absorption coefficient in terms of the quasistatic variant of the line wing theory. Therefore, new parameters of the quantum potential⁸ $U(r, \Omega)$ (Ω are the angular variables characterizing molecule orientation), specified in

analytical form, were found from the condition of proper description of experimental data on H₂O absorption coefficient within a range 300–1100 cm⁻¹ at $T = 296$ K. This potential was used in Ref. 8 for calculation of the second virial coefficient.

Note, that our actions according to the scheme, described in Section 3, have resulted in the classical potential, which does not allow data description by temperature dependences of the second virial coefficient (Fig. 3). The reason can well be an additional physical factor, existing for the wing of the H₂O molecule rotational band,^{2,15} i.e., the effect of spatial dispersion of the imaginary part of dielectric permittivity, which is of high interest. Changes appear already in the definition itself of the absorption coefficient and result in the additional multiplier $\Phi(\omega)$ in Eq. (5).

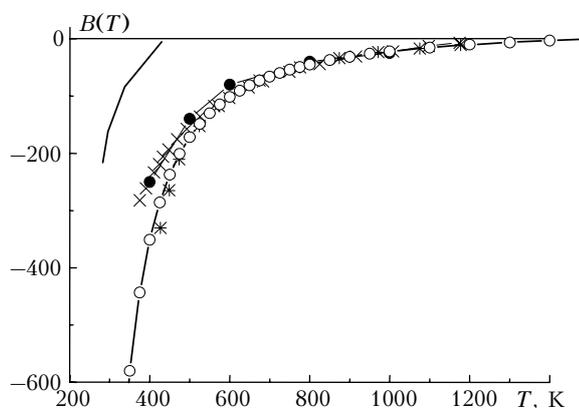


Fig. 3. The second virial coefficient for water vapor as a function of temperature: \times corresponds to calculated data from Ref. 8; \bullet is the data,⁹ calculated with the temperature dependent Lennard–Jones potential; $*$ and \circ correspond to experimental data from Refs. 10 and 11; — is the data, calculated by the scheme from Section 3.

In other words, the data on potentials of intermolecular interactions are to be obtained by the previous scheme, but from the function κ/Φ . Unfortunately, the present model¹⁵ ensures only rather qualitative elements Φ . The question of whether some information about this value can be found is of interest as an argument for existing of the discussed effect itself.

The only qualitative analysis is oriented to the most common model elements. According to the model, the additional multiplier $\Phi \rightarrow 1$ with the temperature decrease; therefore, being determined at the lowest “experimental” temperature and with V from the virial coefficient, it is expected to be the closest to the real one. If then to calculate with such Φ the absorption coefficient (5) at a higher temperature (with the corresponding V), then Φ can be presented as the ratio of the experimental absorption coefficient to the previous estimate. According to the model, $\Phi < 1$. This is demonstrated by curve 1 in Fig. 4.

As an alternative variant, quantum potential is obtained from the absorption coefficient at a high temperature, which gives curve 2 in Fig. 4. In fact

this evidences an essential role of the quantum potential, that is not surprising, as it formalizes the Fermi golden rule.

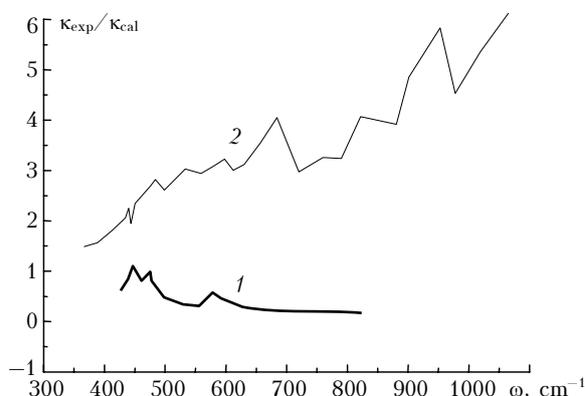


Fig. 4. Φ definition in the absorption coefficient due to the effect of spatial dispersion of the imaginary part of dielectric permittivity as the ratio of experimental and calculated absorption coefficients, obtained at 296 and 430 K at different quantum and classical potentials.

Return to the “spectroscopic” second virial coefficient (considering the 8–12 μm range) for water molecules, calculated in Ref. 8. The used method virtually ignores the difference between quantum and classical potentials: when calculating $\tilde{r}(\omega, \omega_0)$ analog, the model potential is selected so that to describe the spectral (throughout the considered range) absorption coefficient for 296 K, and then the same potential is used both in the Boltzmann multiplier and in constructing the temperature dependence of the second virial coefficient. This dependence is in a good agreement with data for sufficiently high temperature, but has some noticeable difference with those for the “initial” temperature 296 K (see Fig. 3).

The results of Ref. 8 are quite interesting in a (possibly) some unexpected sense. The analysis of the used resolvent conversion method from the viewpoint of mathematically exact perturbation theory convinces that its use is virtually equivalent to classical description of the molecule rotation. A relative success of Ref. 8 can be evident of possible efficiency of such approximation in the theory of rotational lines profile.

Conclusion

The method of semiclassical representation, being valuable for the theory of periphery of spectral line profile, is applicable for calculation of thermodynamic parameters of a medium. This fact allows a discussion of a correlation between spectroscopic and thermodynamic parameters, comparing results of completely independent experiments. In its turn, this gives, firstly, a good chance to test approximations of the theory of line profiles and, secondly, to essentially simplify calculations for recovering the classical potential from the temperature dependence of the second virial coefficient, using the classical approximation for rotational degrees of freedom when

constructing the quantum potential of intermolecular interactions.

Qualitative indications of spatial dispersion of absorption coefficient in the atmospheric “transparency window” are also important. Such effect, as is ascertained from Refs. 2 and 15, results in local thermodynamic imbalance.

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References

1. E.P. Gordov and S.D. Tvorogov, *Method of Semiclassical Representation of Quantum Theory* (Nauka, Novosibirsk, 1984), 167 pp.
2. L.I. Nesmelova, O.B. Rodimova, and S.D. Tvorogov, *Spectral Line Profile and Intermolecular Interaction* (Nauka, Novosibirsk, 1986), 216 pp.
3. L.I. Nesmelova, O.B. Rodimova, and S.D. Tvorogov, *Atmos. Oceanic Opt.* **5**, No. 9, 609–614 (1992).
4. S.D. Tvorogov and O.B. Rodimova, *J. Chem. Phys.* **102**, No. 22, 8736–8745 (1995).
5. J. Girshfelder, Ch. Kertiss, and R. Berd, *Molecular Theory of Gases and Liquids* [Russian translation] (Foreign Literature Press, Moscow, 1961), 930 pp.
6. B.H. Winters, S. Silverman, and W.S. Benedict, *J. Quant. Spectrosc. and Radiat. Transfer* **4**, No. 4, 527–537 (1964).
7. D.E. Burch, D.A. Gryvna, R.R. Patty, and Ch.E. Bartky, *J. Opt. Soc. Am.* **59**, No. 3, 267–280 (1969).
8. Q. Ma and R.H. Tipping, *J. Chem. Phys.* **116**, No. 10, 4102–4115 (2002).
9. O. Singh and A.W. Joshi, *Pramana* **15**, No. 5, 407–412 (1980).
10. J.R. Reimers, R.O. Watts, and M.L. Klein, *Chem. Phys.* **64**, 95–114 (1982).
11. A.H. Harvey and E.W. Lemmon, *J. Phys. and Chem. Ref. Data* **33**, No. 1, 369–376 (2004).
12. K.E. Mac Cormack and W.G. Schneider, *J. Chem. Phys.* **19**, No. 7, 849–855 (1951).
13. R.S. Dadson, E.J. Evans, and J.H. King, *Proc. Phys. Soc.* **92**, P. 4, No. 578, 1115–1121 (1967).
14. D. Cook, *Can. J. Chem.* **35**, No. 3, 268–275 (1957).
15. L.I. Nesmelova, S.D. Tvorogov, and V.V. Fomin, *Spectroscopy of Line Wings* (Nauka, Novosibirsk, 1977), 141 pp.