

# A chemist's perspective on van der Waals dispersion forces: Challenges and opportunities

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University of Luxembourg

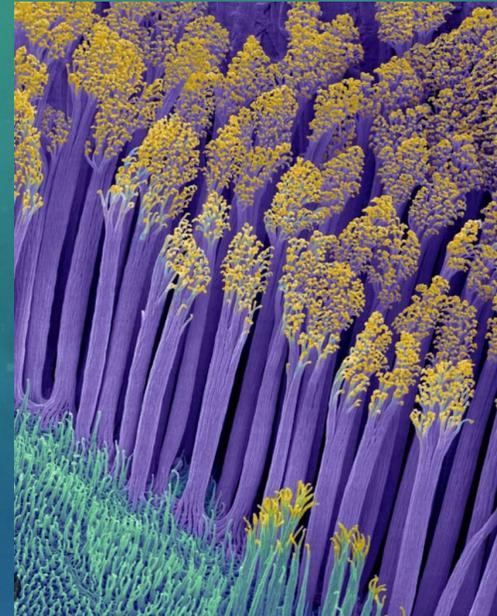
QuFiCh Workshop, October 10, 2023



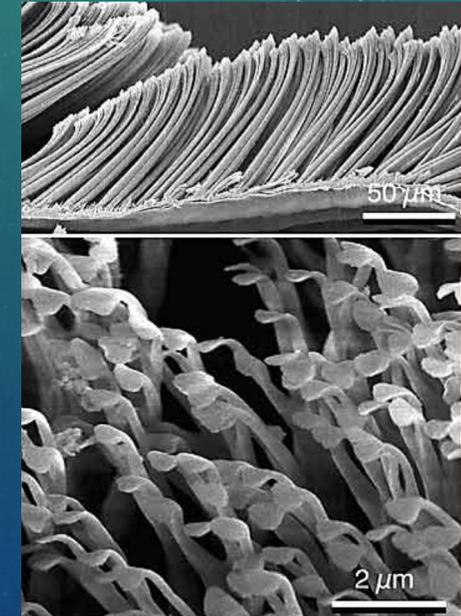
# Van der Waals forces: Ubiquitous noncovalent forces of attraction between molecules



[www.openaccessgovernment.org/wp-content/uploads/2022/07/dreamstime\\_m\\_45071438-1536x1024.jpg](http://www.openaccessgovernment.org/wp-content/uploads/2022/07/dreamstime_m_45071438-1536x1024.jpg)



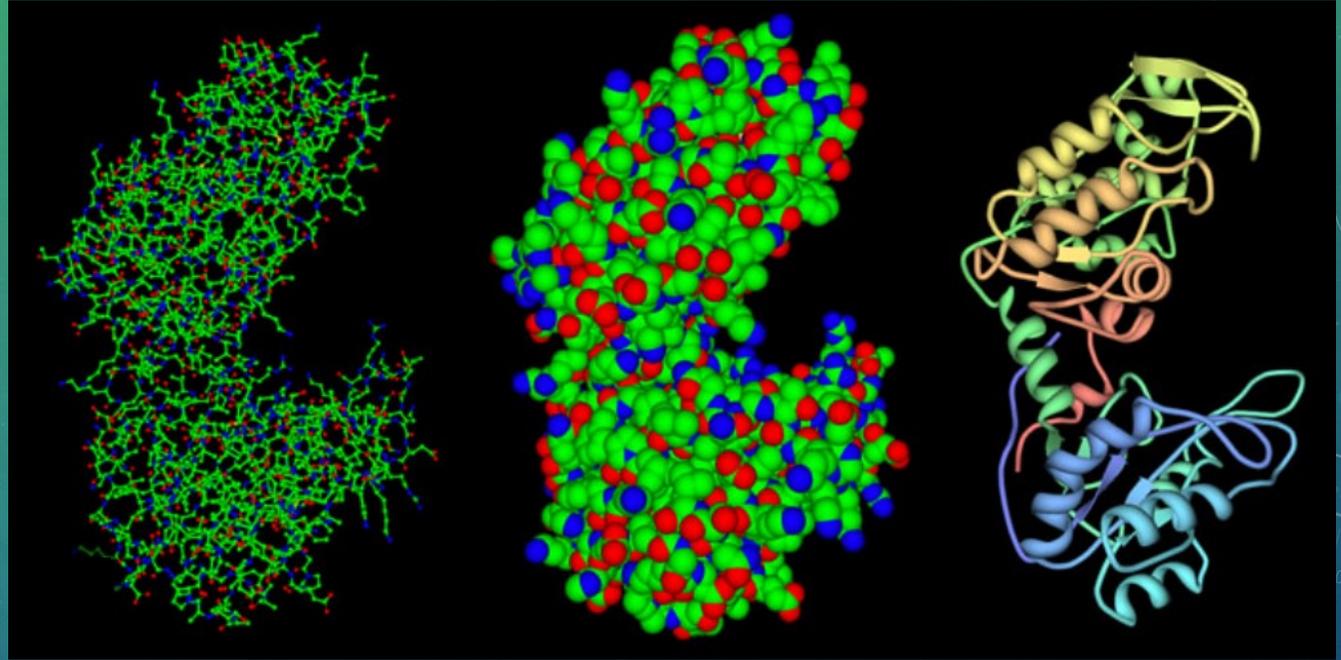
Zeiss Microscopy, in an exhibit by ASCB and the National Institute of General Medical Sciences  
[www.flickr.com/photos/zeissmicro/14255992540](http://www.flickr.com/photos/zeissmicro/14255992540)



[image.jimcdn.com/app/cms/image/trans/dimension=420x1024:format=jpg/path/s53cf316ee29330af/image/icbda63d05ee283a/version/1335978863/image.jpg](http://image.jimcdn.com/app/cms/image/trans/dimension=420x1024:format=jpg/path/s53cf316ee29330af/image/icbda63d05ee283a/version/1335978863/image.jpg)



Achim Oesert, University of Kiel, hangs from the ceiling on biologically inspired tape, 20 cm x 20 cm

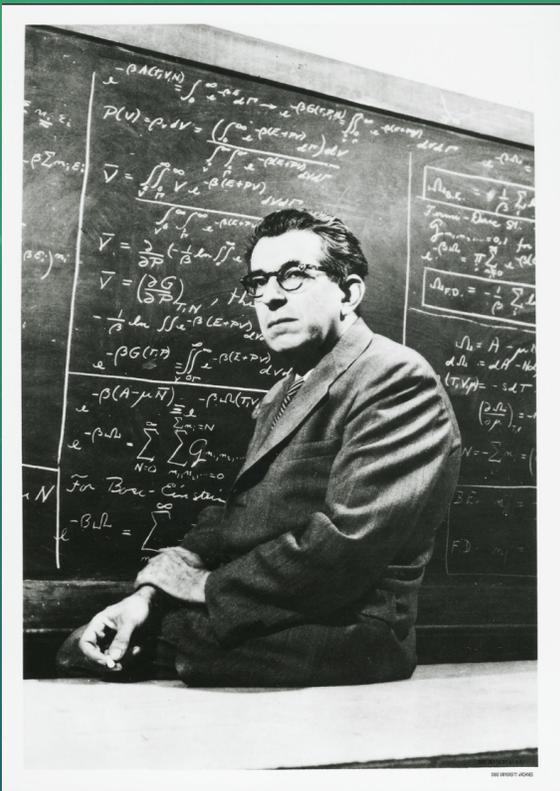


Van der Waals forces contribute significantly to the tertiary structure of proteins, due to nonbonding interactions between amino-acid side chains.

Graphic from PDB 101: A Guide to Understanding Protein Database Data

Biologically inspired tape: project leader Stanislav Gorb, University of Kiel. Tape uses tiny hairs of silicone. Works underwater!

# Covalent and non-covalent interactions



Fritz London,  
Duke University



Walter Heitler, National  
Portrait Gallery, London

Covalent bonding, first quantum  
mechanical theory:  
W. Heitler and F. London,  
*Zeitschrift für Physik* **44**, 455  
(1927).

Dispersion forces, first quantum  
mechanical theory:  
F. London, *Zeitschrift für Physik*  
**63**, 245 (1930).

R. G. Parr, *Physics Today* **54**, 63  
(2001): “the astounding papers  
of Fritz London”

“Sometimes it seems to me that a bond between two atoms has become so real, so tangible, so friendly, that I can almost see it. Then I awake with a little shock, for a chemical bond is not a real thing. It does not exist. No one has ever seen one. No one ever can. It is a figment of our own imagination.” Charles A. Coulson, Oxford

# Elementary quantum mechanical approach to dispersion forces

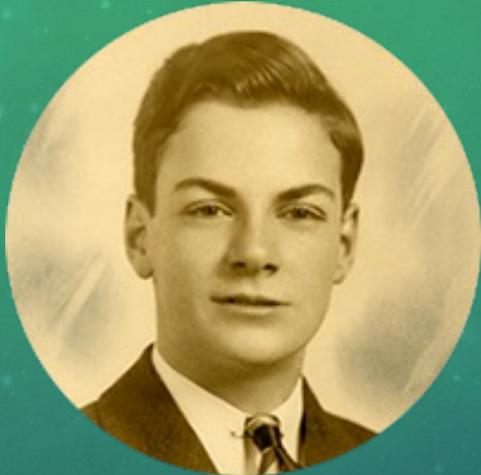
Rayleigh-Schrodinger perturbation theory, polarization approximation

$$\Delta E_{\text{disp}} = \sum_{n \neq 0} \sum_{m \neq 0} \frac{|\langle \Psi^A_0 \Psi^B_0 | V^{AB} | \Psi^A_n \Psi^B_m \rangle|^2}{(E^A_0 + E^B_0 - E^A_n - E^B_m)}$$

If the leading term in  $V^{AB}$  represents dipole-dipole interactions, we obtain  $\Delta E = -C_6 R^{-6} + \dots$  with the dispersion coefficient  $C_6$  (in atomic units),

$$C_6 = (3/\pi) \int_0^\infty \alpha^A(i\omega) \alpha^B(i\omega) d\omega$$

# Interpretation of dispersion forces by Richard Feynman



© Estate of  
Richard Feynman



John C. Slater, AIP  
Physics History Network

**1939:** R. P. Feynman, Forces in Molecules, *Physical Review* **56**, 340.

“Van der Waals forces can also be interpreted as arising from charge distributions with higher concentrations between the nuclei. The Schrodinger perturbation theory for two atoms at a separation  $R$ , large compared to the radii of the atoms, leads to the result that **the charge distribution of each is distorted from central symmetry, a dipole moment of order  $1/R^7$  being induced in each atom.** The negative charge distribution of each atom has its center of gravity moved slightly toward the other. It is not the interaction of these dipoles which leads to van der Waals’ force, but rather the **attraction of each nucleus for the distorted charge distribution of its own electrons that gives the attractive  $1/R^7$  force.**”

Numerical tests of Feynman's statement were not successful until 1967 . . . then only for two H atoms, initially in the 1s state! Impossible then for any heavier atoms, due to numerical errors.

J. O. Hirschfelder and M. A. Eliason, *J. Chem. Phys.* **47**, 1164 (1967).

“Our calculations verify the *conjecture* which Feynman made in his original paper.”

$$\Psi = \Psi_0 + \Psi_3 R^{-3} + \Psi_4 R^{-4} + \Psi_5 R^{-5} + \Psi_6 R^{-6} + \Psi_7 R^{-7} + \dots$$

93% of the  $C_6$  coefficient is due to the  $R^{-7}$  term in the wave function.

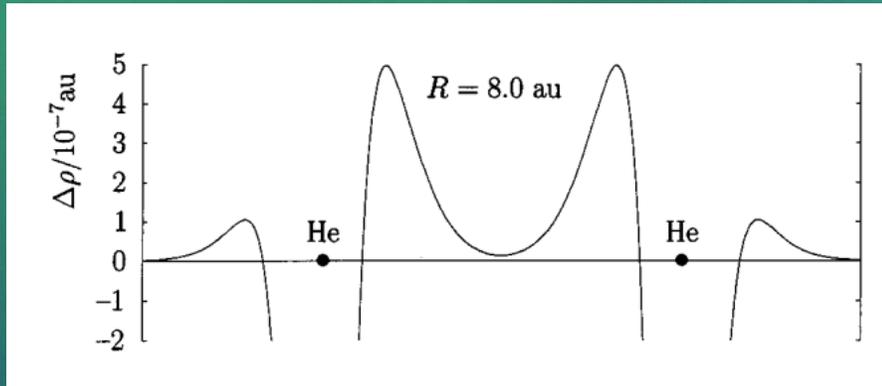
Total force constant from the electrostatic Hellmann-Feynman theorem:

39.001 a.u.

Accurate result: 38.99418 a.u.

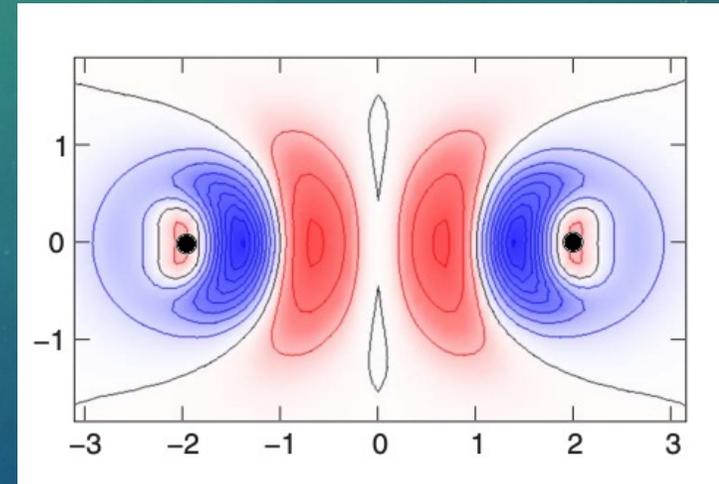
# Studies on heavier diatomics

2002: M. J. Allen and D. J. Tozer,  
*J. Chem. Phys.* **117**, 11113.  
He . . . He



Brueckner coupled cluster calculations. Differences between the forces calculated with the BD(T) densities and the known long-range dispersion forces are 11% at 8.0 a.u., 8.8% at 8.5 a.u. and -4.5% at 9.0 a.u. From DFT (ZMP), 17%, 12% and 9%.

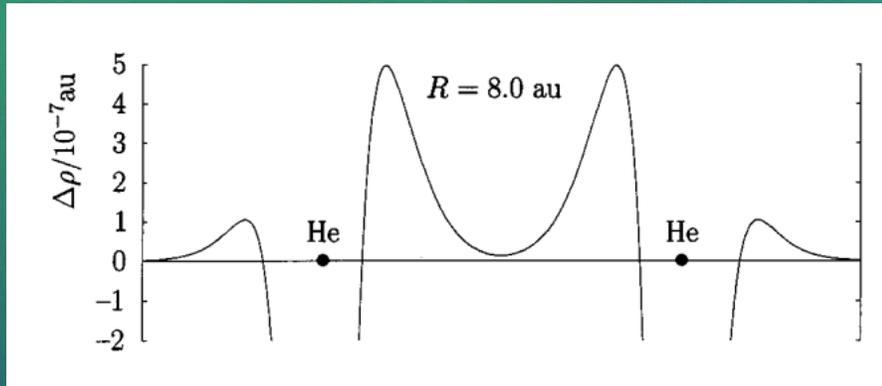
2007: T. Thonhauser, V. R. Cooper, S. Li,  
A. Puzder, P. Hyldgaard, and D. Langreth,  
*Phys Rev. B* **76**, 125112. Ar . . . Ar



Axis labels in a.u., contour interval  $5 \cdot 10^{-5} \text{ e}^{-}/\text{\AA}^3$   
Excellent agreement between Hellmann-Feynman forces and forces from energy derivatives, based on a nonlocal density functional for Ar . . . Ar and Kr . . . Kr; but no comparison is made with the accurate long-range results.

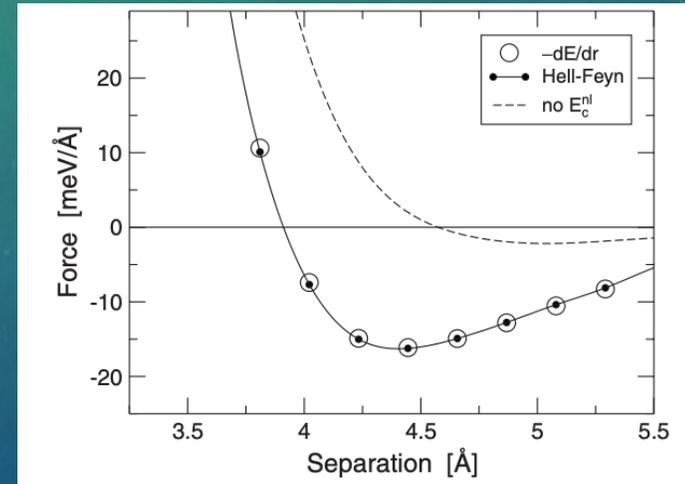
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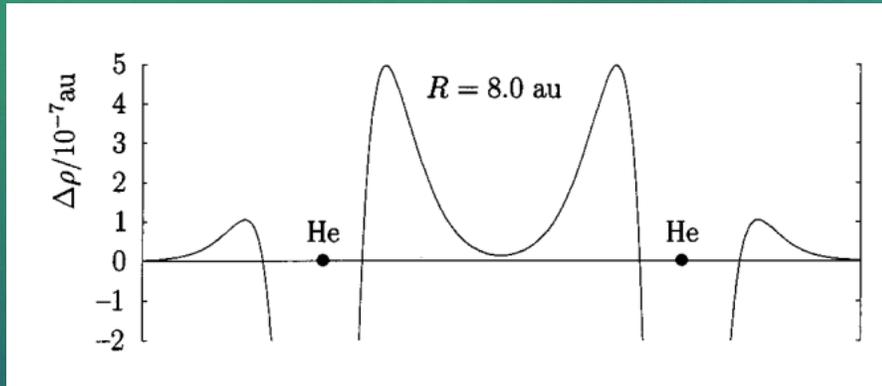
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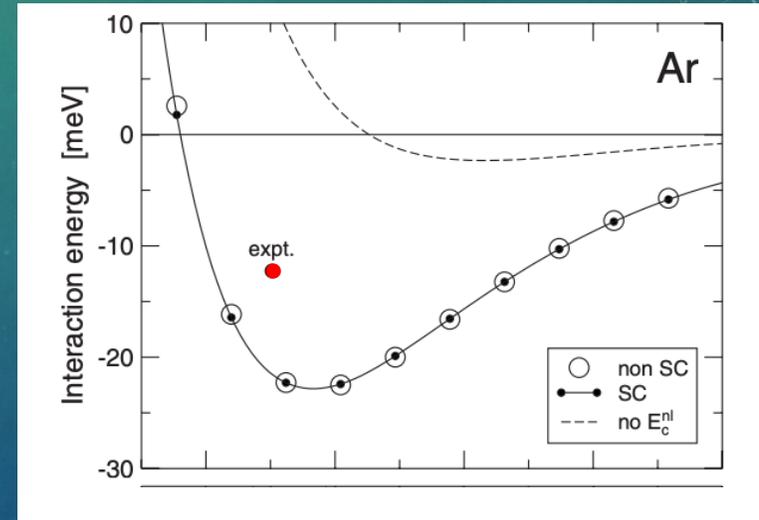
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Dipole moment of two atoms at long range, due to dispersion forces

$$\mu_z^{AB} = (9\hbar R^{-7}/\pi) \int_0^\infty [ \alpha^A(i\omega) B^B(0,i\omega) - \alpha^B(i\omega) B^A(0,i\omega) ] d\omega$$

$B^X(0,i\omega)$  denotes the dipole-dipole-quadrupole hyperpolarizability of atom X

$\alpha^X(i\omega)$  denotes the polarizability of atom X

If  $\mu_z^{AB}$  is positive, the polarity of the dispersion dipole is  $A^+B^-$

Physical mechanisms in the chemists' view:

- 1) Each atom is hyperpolarized by the fluctuating charge distribution of the neighboring atom, and the applied field
- 2) The applied field alters spontaneous quantum fluctuations of the atomic charge densities

L. Galatry and T. Gharbi, *Chem. Phys. Lett.* **75**, 427 (1980).

K. L. C. Hunt and J. E. Bohr, *J. Chem. Phys.* **83**, 5198 (1985).

## Dispersion dipole of atom A in the presence of B

Consider the hyperpolarization of A by the applied field and the field-gradient of the fluctuating dipole of B. Also, consider the dipole-quadrupole fluctuation correlations induced in A by the applied field. For  $H \ll H_c$ , both of these responses can be viewed as localized to atom A or atom B, giving

$$\begin{aligned}\mu_z^{A(B)} &= -9\hbar R^{-7}/\pi \int_0^\infty [\alpha^B(i\omega) B^A(0,i\omega)] d\omega \\ &= -394.51 R^{-7}\end{aligned}$$

Evaluation by 64-point Gaussian quadrature, using values of  $B^A(0,i\omega)$  and  $\alpha^B(i\omega)$  tabulated by David Bishop and Janusz Pipin.

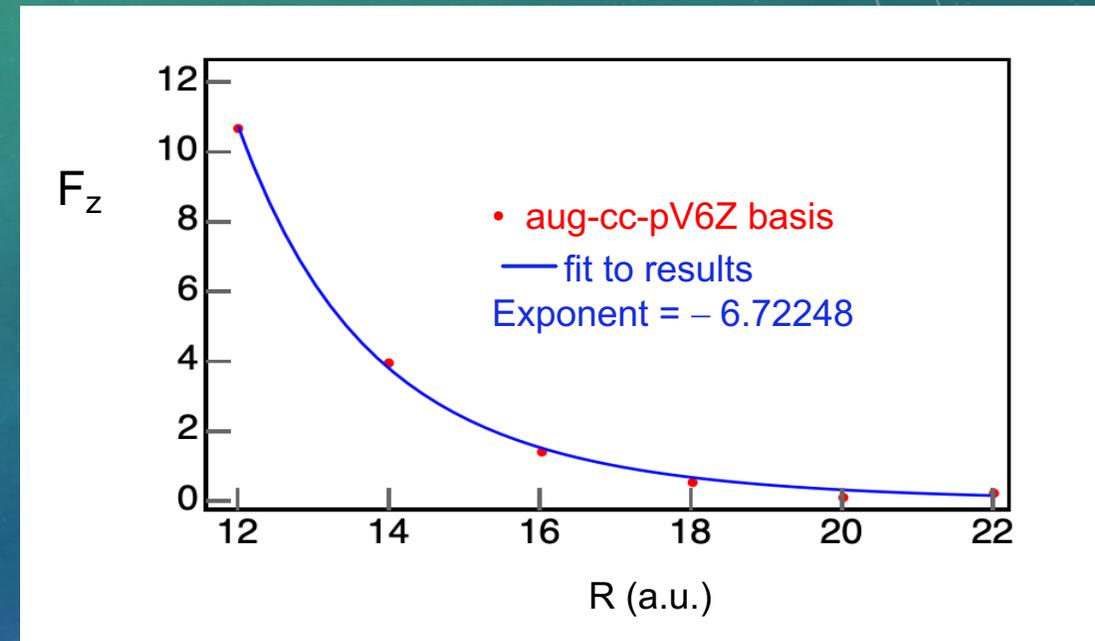
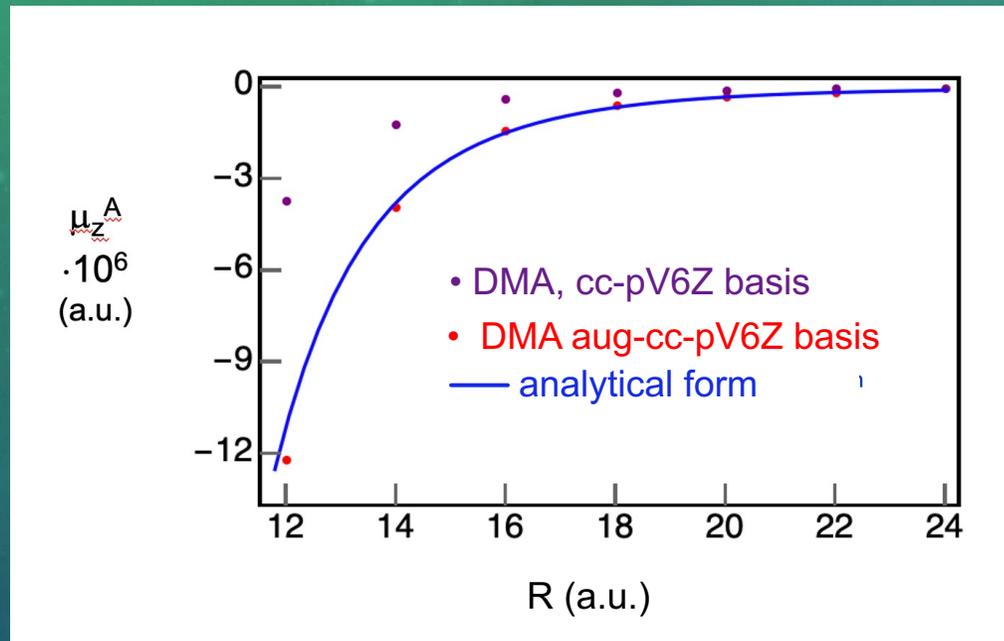
D. M. Bishop and J. Pipin, *Int. J. Quantum Chem.* **45**, 349 (1993).

D. M. Bishop and J. S. Pipin, *J. Chem. Phys.* **98**, 4003 (1993).

# Dispersion dipole and dispersion force for H<sub>2</sub> in the triplet state

Results from the charge densities

Full configuration-interaction calculations, including exchange



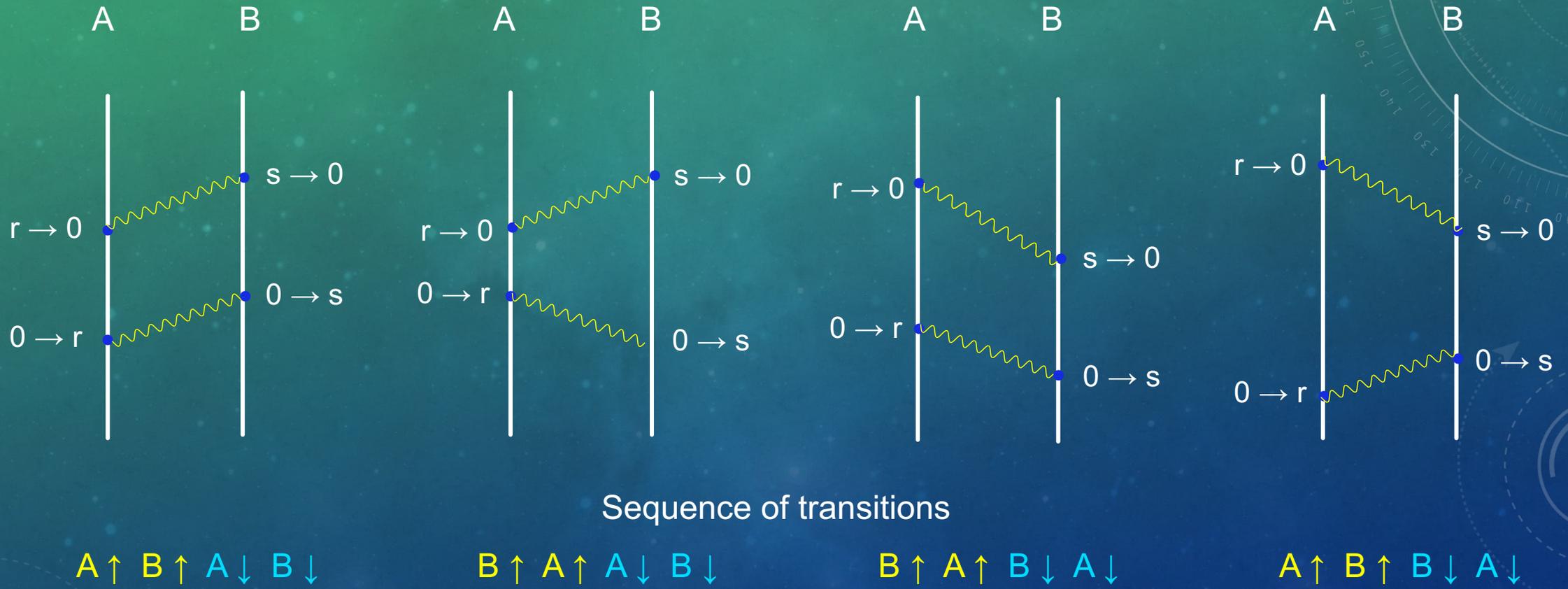
210 basis functions

Force:  $6 C_6 R^{-7}$ ,  $6 C_6 = 38.542$  (this work), 39.001 (H&E), 39.994 (exact), in a.u.

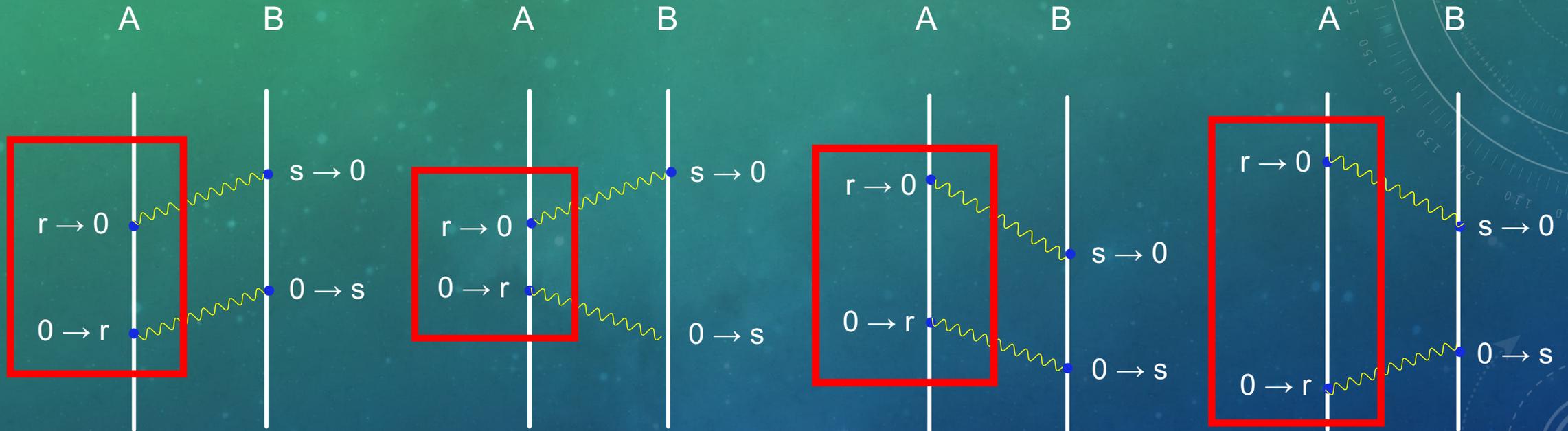
3.63% difference, possibly due to exchange effects

N. D. Jansen and K. L. C. Hunt (work in progress, 2023)

# Significant diagrams contributing to the dispersion energy in the near zone (van der Waals dispersion)



In a static external electric field, how do the field-induced fluctuation correlations enter? For molecule A, they must be within the red boxes.



Sequence of transitions

A ↑ B ↑ A ↓ B ↓

B ↑ A ↑ A ↓ B ↓

B ↑ A ↑ B ↓ A ↓

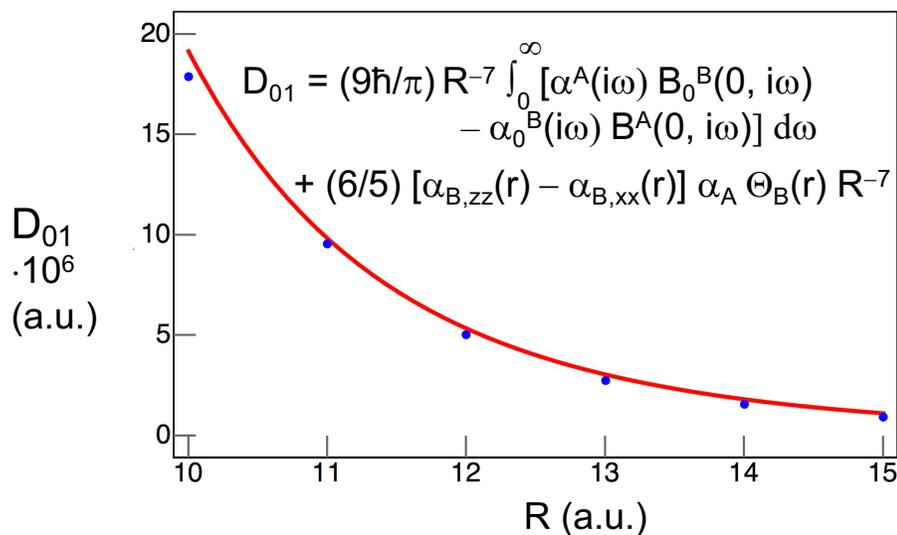
A ↑ B ↑ B ↓ A ↓

Can we see the dispersion dipole directly in *ab initio* quantum calculations?

Example: Interaction-induced dipole of  $\text{H}_2 \cdots \text{H}$

$$\mu^M(r, R, \theta) = 4\pi/3^{1/2} \sum_{\lambda, L, m} D_{\lambda L}(r, R) \langle \lambda L m M - m | 1 M \rangle Y_{\lambda}^m(\theta, \phi) Y_L^{M-m}(0, 0)$$

$D_{01}$  converges to the known long-range form!



Dispersion plus back induction, aug-cc-pV5Z basis with correction for basis-set extension errors (BSSE)

Hunt & Bohr (1987); Bishop & Pipin (1992)  
H.-K. Lee, X. Li, E. Miliordos, and K. L. C. Hunt, *J. Chem. Phys.* **150**, 204307 (2019).

Leading term in the dispersion dipole for a pair of  $T_d$  molecules

$$\mu_j^{AB} = -(3\hbar R^{-6}/2\pi) \int_0^\infty [\alpha^A(i\omega) \beta^B(0,i\omega) g_j^B - \alpha^B(i\omega) \beta^A(0,i\omega) g_j^A] d\omega$$

$\beta^X(0,i\omega)$  denotes the first hyperpolarizability of atom X, which accounts for frequency doubling; j is a Cartesian axis.

$g_j^X$  is a geometric factor. Unit vectors along the  $C_2$  axes of the  $T_d$  molecules are denoted by i, j, and k, and  $u = \mathbf{R}/R$ . Then

$$g_j^X = (i^X \cdot u) (j^X \cdot u) k_j^X + (i^X \cdot u) (k^X \cdot u) j_j^X + (j^X \cdot u) (k^X \cdot u) i_j^X$$

L. Galatry and A. Hardisson, *J. Chem. Phys.* **79**, 1758 (1983).

# Questions remaining about Feynman's "conjecture"



Portrait by Sylvia Posner, 1981

Claim: The dispersion force between 2 atoms in S states is caused by the attraction of each nucleus to its "own" electrons.

For atoms and centrosymmetric molecules,

$$\mu_{\text{disp}} \sim R^{-7} \text{ and } F_{\text{disp}} \sim R^{-7}$$

But for a non-centrosymmetric molecule,  $\mu_{\text{disp}} \sim R^{-6}$  while  $F_{\text{disp}} \sim R^{-7}$

But linear response gives  $E_{\text{disp}}$  while *nonlinear* response is needed to obtain  $\mu_{\text{disp}}$

## A (somewhat) unexpected connection

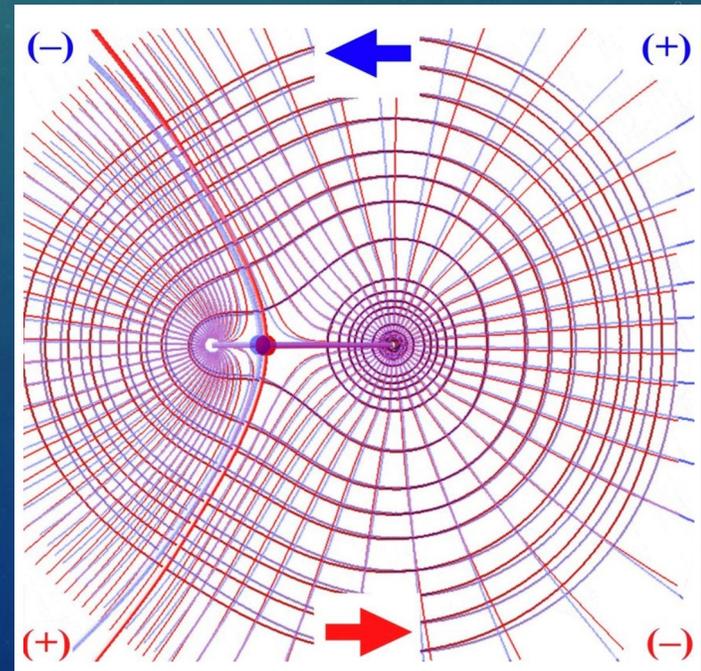
In a static applied field  $F_e$ , the electrons redistribute.

$$F^J = F^{(0)}(R^J) + F_e(R^J) + \int T(R^J, r) \cdot P_{\text{ind}}(r) dr + \dots$$
$$= F^{(0)}(R^J) + F_e(R^J) + \int T(R^J, r) \cdot \alpha(r, r') dr dr' + \dots$$

$$F_J = F^{(0)}(R^J) + (1 - \gamma^J) \cdot F_e + \dots$$

$$\gamma_{\alpha\beta}^J = - \int T(R^J, r)_{\alpha\delta} \alpha_{\delta\beta}(r, r') dr dr'$$

Illustration: S. S. Hashjin, M. Kartunnen, and C. F. Matta, *J. Phys. Chem. A* **124**, 4720 (2020). Electron density contour maps for HCl in fields of  $1.03 \cdot 10^{10}$  V/m (0.02 a.u.) parallel (blue) or antiparallel (red) to the permanent dipole moment



A (somewhat) unexpected connection, completed

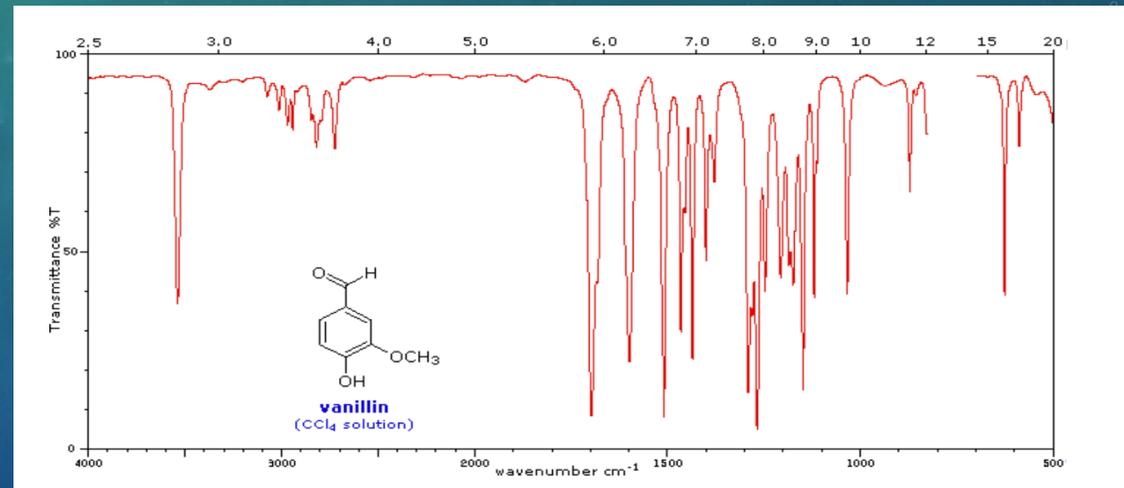
The dipole derivative with respect to a normal mode coordinate determines the intensity of absorption bands in the infrared. It is connected to the Sternheimer shielding tensor,  $\gamma^J_{\alpha\beta}$  for nucleus J

P. Lazzeretti and R. Zanasi, *Chem. Phys. Letters* **112**, 103 (1984):

$$\gamma^J_{\alpha\beta} = Z^J \delta_{\alpha\beta} - \partial\mu_\beta / \partial R^J_\alpha$$

When a nucleus shifts, the change in the dipole moment is also governed by the nonlocal polarizability density

Vanillin spectrum from <https://www2.chemistry.msu.edu/faculty/reusch/virttxtjml/spectrpy/infrared/infrared.htm>



K. L. C. Hunt, *J. Chem. Phys.* **90**, 4909 (1989):

$$\partial\mu_\alpha / \partial R^J_\beta = Z^J \delta_{\alpha\beta} + Z^J \int \alpha_{\alpha\gamma}(r, r') T(R^J, r)_{\gamma\beta} dr dr'$$

## Route to an analytical proof

Work with the polarization operator,  $P(\mathbf{r})$ , such that  $\nabla \cdot P(\mathbf{r}) = -\rho(\mathbf{r})$ .

$\alpha(\mathbf{r}, \mathbf{r}', \omega)$  gives the polarization induced at point  $\mathbf{r}$  by an applied field,

$$P(\mathbf{r}, \omega) = \int \alpha(\mathbf{r}, \mathbf{r}', \omega) \cdot F(\mathbf{r}', \omega) d\mathbf{r}'$$

Connection between permanent moments and linear response

$$\partial\mu_{\alpha}/\partial R^J_{\beta} = Z^J \delta_{\alpha\beta} + Z^J \int \alpha_{\alpha\gamma}(\mathbf{r}, \mathbf{r}') T(R^J, \mathbf{r})_{\gamma\beta} d\mathbf{r} d\mathbf{r}'$$

K. L. C. Hunt, *J. Chem. Phys.* **78**, 6149 (1983).

K. L. C. Hunt, *J. Chem. Phys.* **90**, 4909 (1989).

P. S. Venkataram, J. Hermann, T. J. Vongkovit, A. Tkatchenko, and A. W. Rodriguez, *Science Advances* **5**, eaaw0456 (2019).

J. Hermann and A. Tkatchenko, *Phys. Rev. Lett.* **124**, 146401 (2020).

Szabolcs Góger, Ph.D. Thesis, University of Luxembourg, 2023

## Connection between linear and nonlinear response

$$\partial \alpha_{\alpha\beta}(\mathbf{r}, \mathbf{r}'; \omega) / \partial R_{\gamma}^J = Z^J \int \beta_{\alpha\beta\delta}(\mathbf{r}; \mathbf{r}', \omega; \mathbf{r}'', 0) T_{\delta\gamma}(R^J, \mathbf{r}'') d\mathbf{r}''$$

### Higher-order connection

$$\begin{aligned} \partial \beta_{\alpha\beta\gamma}(\mathbf{r}, -\omega_{\sigma}; \mathbf{r}', \omega_1; \mathbf{r}'', \omega_2) / \partial R_{\delta}^J \\ = Z^J \int \gamma_{\alpha\beta\gamma\epsilon}(\mathbf{r}, -\omega_{\sigma}; \mathbf{r}', \omega_1; \mathbf{r}'', \omega_2, \mathbf{r}''', 0) / T_{\epsilon\delta}(R^J, \mathbf{r}''') d\mathbf{r}''' \end{aligned}$$

K. L. C. Hunt, *J. Chem. Phys.* **90**, 4909 (1989).

K. L. C. Hunt, Y. Q. Liang, R. Nimalakirithi, and R. A. Harris, *J. Chem. Phys.* **91**, 5251 (1989).

E. L. Tisko, X. Li, and K. L. C. Hunt, *J. Chem. Phys.* **103**, 6873 (1995).

# Proof of Feynman's "conjecture" in the polarization approximation

## Physical mechanism (again, a chemist's view)

- Spontaneous, quantum mechanical fluctuations in the charge density of molecule A set up a nonuniform local field at B.\*
- The local field induces charge moments in B, as determined by the susceptibilities of B and the nonuniformity of the local field.
- The induced polarization in B gives rise to a nonuniform local field at A, the reaction field.

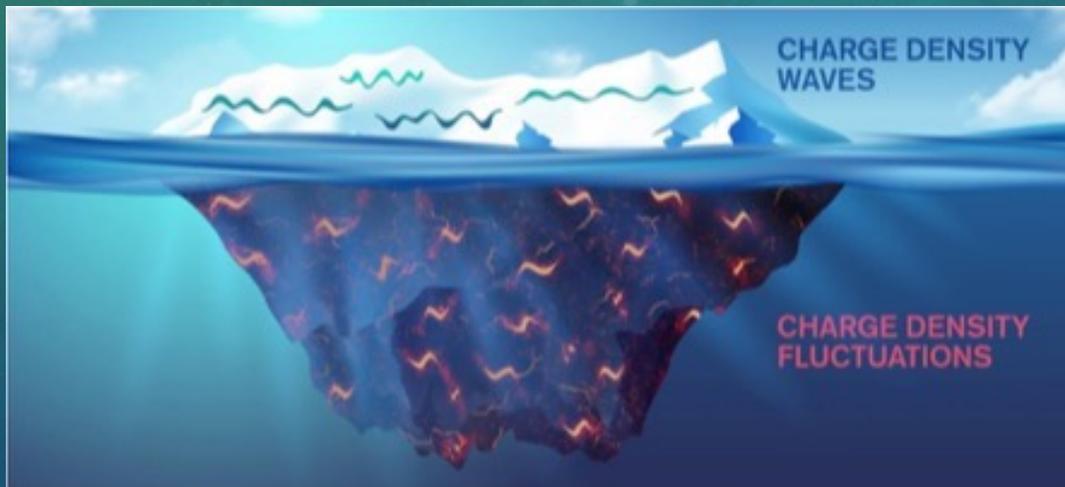
### Reaction field theory:

B. Linder, *Adv. Chem. Phys.* **12**, 225 (1967).

D. Langbein, *Theory of van der Waals Attraction* (Springer, New York, 1974) Chapter 3.

- The resulting energy change in A depends on the correlations of the fluctuating charge moments on A.\*
- The correlations are given by the fluctuation-dissipation theorem of H. B. Callen and T. Welton, *Phys. Rev.* **83**, 34 (1951).\*

$$\begin{aligned}
 & (1/2) \langle P_\alpha(r, \omega) P_\beta(r', \omega') + P_\beta(r', \omega') P_\alpha(r, \omega) \rangle \\
 & = (\hbar/2\pi) \alpha_{\alpha\beta}''(r, r', \omega) \delta(\omega + \omega') \coth(\hbar\omega/2kT)
 \end{aligned}$$



Credit: Yen Strandqvist  
Chalmers University of  
Technology  
In AAAS Eureka Alert!

- The effects of a spontaneous fluctuation in the charge density of B are added.

- The net energy change is given in terms of an integral over all real frequencies.
- The integral is converted to a complex contour integral and evaluated using the residue theorem.
- The susceptibilities are analytic in the upper half plane, to ensure causality. The poles come from the function  $\coth(\hbar\omega/2kT)$ . They are located along the imaginary axis at  $\omega_n = 2\pi i nkT/\hbar$ . Typically, these are sufficiently close together that the sum over the poles can be converted to an integral over imaginary frequencies.

Result for the dispersion energy:

$$\Delta E = -\hbar/2\pi \int_0^\infty d\omega \int \alpha^A_{\delta\alpha}(r; r''', i\omega) T_{\alpha\beta}(r''', r'') \alpha^B_{\beta\gamma}(r''; r', i\omega) T_{\gamma\delta}(r', r) dr dr' dr'' dr'''$$

## Keys to the calculation of the dispersion forces

- The dispersion energy has been obtained in terms of the nonlocal polarizability density. The force on a nucleus is obtained by differentiating with respect to the nuclear coordinate. This will bring the hyperpolarizability density into the expression for the force on the nucleus.
- Separately, the polarization due to dispersion is identified. The approach employs second-order perturbation theory, with the induction and dispersion terms separated. Contributions with **excitations on both centers** are identified as dispersion.
- ... Integral equations, old and new are used, to obtain integrals over products of the susceptibilities on the interacting molecules at imaginary frequencies.

## Outcome

The dispersion term in the polarization of molecule A is

$$\mathbf{P}_{\alpha}^{\text{A}}(r)_{\text{disp}} = (\hbar/2\pi) \int_0^{\infty} \int \beta_{\beta\gamma\alpha}^{\text{A}}(r'; r'', i\omega; r, 0) T_{\gamma\delta}(r'', r''') \\ \alpha_{\delta\varepsilon}^{\text{B}}(r''', r^{\text{iv}}, i\omega) T_{\varepsilon\beta}(r^{\text{iv}}, r') dr' dr'' dr''' dr^{\text{iv}}$$

and the dispersion force on nucleus J is

$$\mathbf{F}_{\varepsilon, \text{disp}}^{\text{J}} = \int \mathbf{P}_{\varphi}^{\text{A}}(r^{\text{iv}})_{\text{disp}} Z^{\text{J}} T_{\varphi\varepsilon}(r^{\text{iv}}, R^{\text{J}}) dr^{\text{iv}}$$

The Feynman "conjecture" holds for molecules of arbitrary symmetry!

K. L. C. Hunt, *J. Chem. Phys.* **92**, 1180 (1990).

# But what about the $R^{-6}$ dipoles and $R^{-7}$ forces for molecules?

Stack Exchange contribution: “Luckily Hunt has shown in a very **laborious** 1990 paper that Feynman’s picture holds true in that case as well.”



## About

Apparently, this user prefers to keep an air of mystery about them.

Generalization of the Thomas-Reiche-Kuhn sum rule

$$\begin{aligned} \text{Quadrupole operator with non-zero trace: } q_{\beta\gamma} &= \int dr P_{\beta}(r) r_{\gamma} + P_{\gamma}(r) r_{\beta} \\ \langle 0 | [p_{\alpha}, q_{\beta\gamma}] | n \rangle &= (\hbar/i) \langle 0 | \mu_{\gamma} | n \rangle \delta_{\alpha\beta} + (\hbar/i) \langle 0 | \mu_{\beta} | n \rangle \delta_{\alpha\gamma} \\ &= \sum_m' \langle 0 | p_{\alpha} | m \rangle \langle m | q_{\beta\gamma} | n \rangle - \langle 0 | q_{\beta\gamma} | m \rangle \langle m | p_{\alpha} | n \rangle \\ &\quad - \langle 0 | q_{\beta\gamma} | n \rangle \langle 0 | p_{\alpha} | n \rangle \end{aligned}$$

Result: In polyatomic molecules, the forces on individual nuclei typical vary as  $R^{-6}$  in the center-to-center separation, but the net force on the center of mass varies as  $R^{-7}$ . The  $R^{-6}$  terms drop out.

But what about the  $R^{-6}$  dipoles and  $R^{-7}$  forces for molecules?

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Generalization of the Thomas-Reiche-Kuhn sum rule

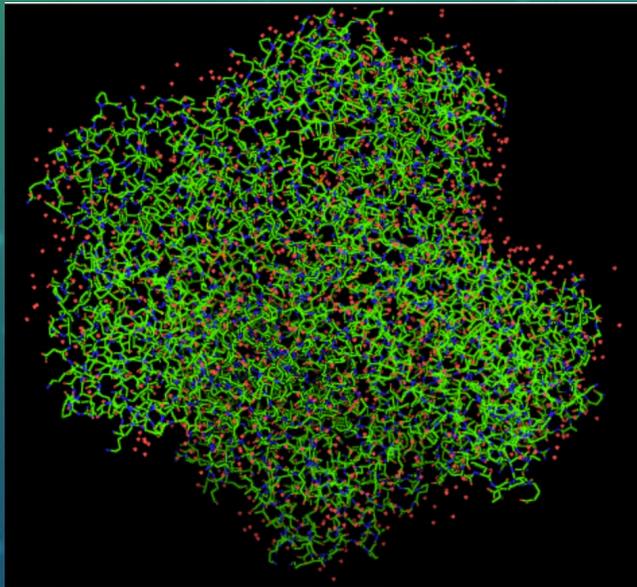
$$\begin{aligned} \text{Quadrupole operator with non-zero trace: } q_{\beta\gamma} &= \int dr P_{\beta}(r) r_{\gamma} + P_{\gamma}(r) r_{\beta} \\ \langle 0 | [p_{\alpha}, q_{\beta\gamma}] | n \rangle &= (\hbar/i) \langle 0 | \mu_{\gamma} | n \rangle \delta_{\alpha\beta} + (\hbar/i) \langle 0 | \mu_{\beta} | n \rangle \delta_{\alpha\gamma} \\ &= \sum_m' \langle 0 | p_{\alpha} | m \rangle \langle m | q_{\beta\gamma} | n \rangle - \langle 0 | q_{\beta\gamma} | m \rangle \langle m | p_{\alpha} | n \rangle \\ &\quad - \langle 0 | q_{\beta\gamma} | n \rangle \langle 0 | p_{\alpha} | n \rangle \end{aligned}$$

Result: In polyatomic molecules, the forces on individual nuclei typical vary as  $R^{-6}$  in the center-to-center separation, but the net force on the center of mass varies as  $R^{-7}$ . The  $R^{-6}$  terms drop out.

# Current Challenges

Dispersion interactions in the presence of a time-dependent applied field?  
Only partially answered, in my view.

Applications to biological systems or materials  
Proteins: many-body dispersion



A mix of near-zone, far-zone and intermediate zone dispersion

Illustration:  
Methionine  
gamma-lyase  
subunit

Aldam, CC BY-SA 4.0  
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via Wikimedia Commons



Ribosome: 20 to 30 nm across  
Animation from  
[https://upload.wikimedia.org/wikipedia/commons/9/94/Protein\\_translation.gif](https://upload.wikimedia.org/wikipedia/commons/9/94/Protein_translation.gif)



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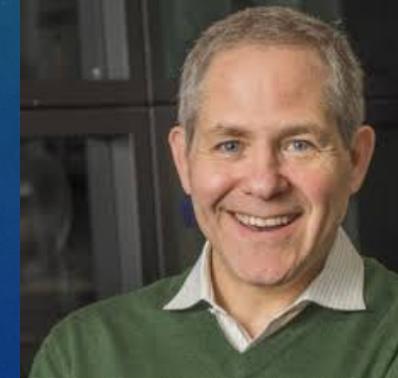
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