

A perspective on the link between the exchange(-correlation) hole and dispersion forces

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Abstract In a recent series of papers, Becke and Johnson have proposed an elegant model for London dispersion (van der Waals') forces in terms of the exchange hole. A perspective on this work is presented here, showing how the exchange-correlation hole is naturally related to "conventional" perturbative approaches to dispersion. The key to establishing this link is the fluctuation-dissipation theorem, which allows the exchange-correlation hole to be related to the frequency-dependent linear response.

1 Introduction

In a recent series of papers, Axel Becke and Erin Johnson have shown how the exchange hole can be used to construct a model for London dispersion forces in molecules [1–7]. The great strength of their work is that it couches dispersion forces in density-functional theoretic language; this offers the prospect of extending DFT to long-range interactions in a more rigorous and less *ad hoc* way than usual [8–12]. The weakness of their work is that the link between dispersion and the multipole moments of the exchange hole is assumed. (However, once this link is assumed, the formulas flow inexorably to the desired end.) Perhaps because of this assumption, and the seemingly mysterious way that the "exchange hole" leads to a "correlation effect," the Becke-Johnson model has inspired some controversy [13]. Still, based on the impressive numerical agreement between the Becke-Johnson models and accurate experimental and computational results for a wide range of van der Waals complexes, it seems that there must be some deep physical and mathematical rationale for the success of their models. The goal of this paper is to provide a framework for understanding that success and, hopefully, constructing even better models.

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It should be mentioned that the present study is very similar to one by Janos Ángyán, [14] who derived his results independently. Interested readers should definitely read his paper, which supersedes this one in (a) explaining the link to conventional methods for approximating dispersion and (b) drawing the link to the specific dispersion model proposed by Becke and Johnson. This paper offers a alternative mathematical perspective, one which some people in density-functional theory may find slightly more familiar, even if (or maybe because) it is less explicit. Specifically, the goal of this paper is to establish the plausibility of general models of the Becke-Johnson type, acknowledging that it may be desirable (and even necessary) to supersede the models in their original papers. In particular, I hope that a more rigorous understanding of the underlying forces may lead to methods that do not require *ad hoc* damping factors to remove the pathological singularities of R^{-6} at small intermolecular separations. In that regard, a recent paper by Ołasz et al. [15] shows that if the Hirshfeld atomic partitioning [16] of the molecular polarizability is used, [17] then damping is not required. That approach suggests, among other things, that a whole-molecule to the key energetic quantities might be possible. Such an approach is the key result of this paper.

2 The link between dispersion and the exchange-correlation hole

2.1 The perturbative formula for the interaction energy and the fluctuation-dissipation theorem

The starting point of this analysis is the standard second-order perturbation theory formula for the dispersion energy,

$$E_{\text{int}}^{(2)} = \frac{-1}{2\pi} \int \int \int \int \frac{1}{|\mathbf{r}_A - \mathbf{r}_B| |\mathbf{r}'_A - \mathbf{r}'_B|} \times \left[\int_0^\infty \chi_A(\mathbf{r}_A, \mathbf{r}'_A, i\omega) \chi_B(\mathbf{r}'_B, \mathbf{r}_B, i\omega) d\omega \right] d\mathbf{r}'_A d\mathbf{r}'_B d\mathbf{r}_A d\mathbf{r}_B. \quad (1)$$

Here $\chi_A(\mathbf{r}'_A, \mathbf{r}_A, \omega)$ and $\chi_B(\mathbf{r}'_B, \mathbf{r}_B, \omega)$ denote the frequency-dependent linear response kernels for two well-separated electronic systems A and B . The frequency-dependent linear response is linked to the exchange-correlation hole through the fluctuation-dissipation theorem, which links fluctuations in one-electron properties to the response of the system to changes in external potential. If the property of interest is the probability of observing an electron at a given point in space, then the fluctuation-dissipation theorem takes the form

$$\begin{aligned} & \left\langle \Psi_0 \left| \left(\sum_{i=1}^N \delta(\mathbf{r}_i - \mathbf{r}_A) - \rho(\mathbf{r}_A) \right) \left(\sum_{j=1}^N \delta(\mathbf{r}_j - \mathbf{r}'_A) - \rho(\mathbf{r}'_A) \right) \right| \Psi_0 \right\rangle \\ &= -\frac{1}{\pi} \int \int \left[\int_0^\infty \chi(\mathbf{r}, \mathbf{r}', i\omega) d\omega \right] \delta(\mathbf{r} - \mathbf{r}_A) \delta(\mathbf{r}' - \mathbf{r}'_A) d\mathbf{r} d\mathbf{r}' \\ & \rho_2(\mathbf{r}_A, \mathbf{r}'_A) + \rho(\mathbf{r}_A) \delta(\mathbf{r}_A - \mathbf{r}'_A) - \rho(\mathbf{r}_A) \rho(\mathbf{r}'_A) = -\frac{1}{\pi} \int_0^\infty \chi(\mathbf{r}_A, \mathbf{r}'_A, i\omega) d\omega \end{aligned} \quad (2)$$

In the second line we have introduced the definition of the electron pair density. The electron pair density may be expressed in terms of the exchange-correlation hole of the fully interacting system (the $\lambda = 1$ limit of the adiabatic connection),

$$\begin{aligned} \rho_2(\mathbf{r}_A, \mathbf{r}'_A) &= \left\langle \Psi_0 \left| \sum_{i=1}^N \sum_{j \neq i}^N \delta(\mathbf{r}_i - \mathbf{r}_A) \delta(\mathbf{r}_j - \mathbf{r}'_A) \right| \Psi_0 \right\rangle \\ &= \rho(\mathbf{r}_A) \rho(\mathbf{r}'_A) \left(1 + h_{xc}^{(\lambda=1)}(\mathbf{r}_A, \mathbf{r}'_A) \right) \end{aligned} \quad (3)$$

Inserting this expression into Eq. 2 and simplifying gives

$$\rho(\mathbf{r}_A) \left[\rho(\mathbf{r}'_A) h_{xc}^{(\lambda=1)}(\mathbf{r}_A, \mathbf{r}'_A) + \delta(\mathbf{r}_A - \mathbf{r}'_A) \right] = -\frac{1}{\pi} \int_0^\infty \chi(\mathbf{r}_A, \mathbf{r}'_A, i\omega) d\omega. \quad (4)$$

The exchange-correlation charge,

$$\rho_{xc}^{(\lambda=1)}(\mathbf{r}'_A | \mathbf{r}_A) = \rho(\mathbf{r}'_A) h_{xc}^{(\lambda=1)}(\mathbf{r}_A, \mathbf{r}'_A), \quad (5)$$

represents the reduction in the probability of observing an electron at \mathbf{r}'_A because of the presence of an electron at \mathbf{r}_A ; it is normalized to minus one. Since this probability represents a deficit of electron density, it is associated with a region in the molecule that is “more positive” than it would be if there was not an electron at \mathbf{r}_A . In this sense, it is reasonable to define

$$q_{xc}^{(\lambda=1)}(\mathbf{r}'_A | \mathbf{r}_A) = -\rho_{xc}^{(\lambda=1)}(\mathbf{r}'_A | \mathbf{r}_A) - \delta(\mathbf{r}_A - \mathbf{r}'_A) \quad (6)$$

as the charge distribution associated with an electron at the point \mathbf{r}_A . The second term represents a negative point charge at \mathbf{r}_A , representing the position of the “reference” electron. The first term in Eq. 6 is the positively charged “hole” in the electron-distribution that shadows the position of the reference electron. Notice that $q_{xc}^{(\lambda=1)}(\mathbf{r}'_A | \mathbf{r}_A)$ arises from the “fluctuation” side of the fluctuation-dissipation identity. Recalling the conventional theory of dispersion forces relies on “fluctuating dipoles” on the interacting subsystems, one should not be surprised that $q_{xc}^{(\lambda=1)}(\mathbf{r}'_A | \mathbf{r}_A)$ is the key quantity in the Becke-Johnson approach to dispersion interactions.

The Becke-Johnson model is related to the idea that the multipole moments of $q_{xc}^{(\lambda=1)}$ are related to the “instantaneous fluctuations” in the electron distribution that are associated with the dispersion interaction. This emerges as a reasonable model when one compares the fluctuation-dissipation theorem derived result,

$$\rho(\mathbf{r}_A) q_{xc}^{(\lambda=1)}(\mathbf{r}'_A | \mathbf{r}_A) = -\frac{1}{\pi} \int_0^\infty \chi(\mathbf{r}_A, \mathbf{r}'_A, i\omega) d\omega, \quad (7)$$

with the interaction energy formula in Eq. 1.

The derivation by Ángyán is also based on the similarity between the interaction energy expression in Eq. 1 and the fluctuation-dissipation theorem expression for the exchange-correlation hole [14].

2.2 Dispersion in terms of q_{xc}

The qualitative “picture” behind the Becke-Johnson model is, in the author’s view, completely justified by the considerations of the preceding section. In particular, the similarity in form between Eqs. 7 and 1 justifies an approach in which one parameterizes the dispersion interaction in terms of the multipole moments of $q_{xc}^{(\lambda=1)}$. Turning this insight into an explicit and useful parameterization requires some approximations.

First, the interaction energy expression must be written so that $q_{xc}^{(\lambda=1)}$ appears explicitly. To this end, define

$$\Delta(\mathbf{r}_A, \mathbf{r}'_A, \mathbf{r}_B, \mathbf{r}'_B) = \int_0^\infty \chi_A(\mathbf{r}_A, \mathbf{r}'_A, i\omega) \chi_B(\mathbf{r}_B, \mathbf{r}'_B, i\omega) d\omega - \frac{1}{\omega_\Delta} \int_0^\infty \chi_A(\mathbf{r}_A, \mathbf{r}'_A, i\omega) d\omega \int_0^\infty \chi_B(\mathbf{r}_B, \mathbf{r}'_B, i\omega) d\omega \quad (8)$$

where ω_Δ is a frequency factor that is required to preserve dimensional correctness. Then,

$$E_{\text{int}}^{(2)} = \frac{-\pi}{2\omega_0} \iiint \iiint \frac{\rho_A(\mathbf{r}_A) q_{A,xc}^{(\lambda=1)}(\mathbf{r}'_A|\mathbf{r}_A) \rho_B(\mathbf{r}_B) q_{B,xc}^{(\lambda=1)}(\mathbf{r}'_B|\mathbf{r}_B)}{|\mathbf{r}_A - \mathbf{r}_B| |\mathbf{r}'_A - \mathbf{r}'_B|} d\mathbf{r}_A d\mathbf{r}'_A d\mathbf{r}_B d\mathbf{r}'_B - \frac{1}{2\pi} \iiint \iiint \frac{\Delta(\mathbf{r}_A, \mathbf{r}'_A, \mathbf{r}_B, \mathbf{r}'_B)}{|\mathbf{r}_A - \mathbf{r}_B| |\mathbf{r}'_A - \mathbf{r}'_B|} d\mathbf{r}_A d\mathbf{r}'_A d\mathbf{r}_B d\mathbf{r}'_B \quad (9)$$

One should choose ω_Δ so that the second term in Eq. 9 is zero.

There are many alternatives to the “additive correction scheme” in Eq. 9. One alternative is a multiplicative correction in the form of an effective interaction strength,

$$E_{\text{int}}^{(2)} = \frac{-\pi}{2} \iiint \iiint \left(\frac{1 + \mathcal{V}(\mathbf{r}_A, \mathbf{r}'_A, \mathbf{r}_B, \mathbf{r}'_B)}{|\mathbf{r}_A - \mathbf{r}_B| |\mathbf{r}'_A - \mathbf{r}'_B|} \right) \rho_A(\mathbf{r}_A) q_{A,xc}^{(\lambda=1)}(\mathbf{r}'_A|\mathbf{r}_A) \rho_B(\mathbf{r}_B) q_{B,xc}^{(\lambda=1)}(\mathbf{r}'_B|\mathbf{r}_B) d\mathbf{r}_A d\mathbf{r}'_A d\mathbf{r}_B d\mathbf{r}'_B \quad (10)$$

Ángyán bases his arguments on a multiplicative form like this one. This paper will focus on the additive form, but the reader should keep in mind that the form in Eq. 10 is probably more useful for deriving corrections to the formulas presented here. The multiplicative form also makes stronger contact with conventional dispersion models [14].

2.3 Approximate formulas from the multipole expansion

The next level of approximation introduces some sweeping assumptions and introduces the multipole expansion. First, the second term in Eq. 9 is assumed to be small (or, at least, qualitatively similar to the first term). Next, the subsystems, A and B , are assumed to be well-separated and far apart. The center of charge of the systems is defined as

$$\mathbf{R}_A = \int \mathbf{r} \rho_A(\mathbf{r}) d\mathbf{r} \quad \mathbf{R}_B = \int \mathbf{r} \rho_B(\mathbf{r}) d\mathbf{r} \quad (11)$$

The vectors from each location to the associated centers are denoted

$$\mathbf{r}_{A0} = \mathbf{r}_A - \mathbf{R}_A \quad \mathbf{r}_{B0} = \mathbf{r}_B - \mathbf{R}_B. \quad (12)$$

The distance between the subsystems is denoted

$$R_{AB} = |\mathbf{R}_{AB}| \quad \mathbf{R}_{AB} = \mathbf{R}_B - \mathbf{R}_A. \quad (13)$$

Inserting

$$\frac{1}{|\mathbf{r}_A - \mathbf{r}_B|} = \frac{1}{R_{AB}} + \frac{\mathbf{R}_{AB} \cdot (\mathbf{r}_{B0} - \mathbf{r}_{A0})}{R_{AB}^3} + \frac{3(\mathbf{R}_{AB} \cdot (\mathbf{r}_{B0} - \mathbf{r}_{A0}))^2 - R_{AB}^2}{2R_{AB}^5} + \dots \quad (14)$$

into Eq. 9 gives rise to the multipole expansion.

Many of the terms in the multipole expansion vanish. Because

$$\begin{aligned} 0 &= \int q_{A,xc}^{(\lambda=1)}(\mathbf{r}'_A | \mathbf{r}_A) d\mathbf{r}'_A = \int \rho_A(\mathbf{r}_A) q_{A,xc}^{(\lambda=1)}(\mathbf{r}'_A | \mathbf{r}_A) d\mathbf{r}_A, \\ &= \int q_{B,xc}^{(\lambda=1)}(\mathbf{r}'_B | \mathbf{r}_B) d\mathbf{r}'_B = \int \rho_B(\mathbf{r}_B) q_{B,xc}^{(\lambda=1)}(\mathbf{r}'_B | \mathbf{r}_B) d\mathbf{r}_B \end{aligned} \quad (15)$$

any term in the integral that does not contain *all four variables*— \mathbf{r}_{A0} , \mathbf{r}'_{A0} , \mathbf{r}_{B0} and \mathbf{r}'_{B0} —is zero. For this reason, the terms of order R_{AB}^{-1} and R_{AB}^{-3} in the multipole expansion both vanish. The lowest-order nonzero term is

$$\begin{aligned} E_{\text{int}}^{(2)} &\approx \frac{-9\pi}{\omega_{\Delta} R_{AB}^{10}} \left(\iint (\mathbf{R}_{AB} \cdot \mathbf{r}_{A0}) (\mathbf{R}_{AB} \cdot \mathbf{r}'_{A0}) \rho_A(\mathbf{r}_A) q_{A,xc}^{(\lambda=1)}(\mathbf{r}'_A | \mathbf{r}_A) d\mathbf{r}_A d\mathbf{r}'_A \right. \\ &\quad \left. \times \iint (\mathbf{R}_{AB} \cdot \mathbf{r}_{B0}) (\mathbf{R}_{AB} \cdot \mathbf{r}'_{B0}) \rho_B(\mathbf{r}_B) q_{B,xc}^{(\lambda=1)}(\mathbf{r}'_B | \mathbf{r}_B) d\mathbf{r}_B d\mathbf{r}'_B \right) \quad (16) \end{aligned}$$

If we rewrite \mathbf{R}_{AB} in terms of the unit vector, $\mathbf{R}_{AB} = R_{AB}\hat{\mathbf{R}}_{AB}$, then

$$E_{int}^{(2)} \approx \frac{-9\pi}{\omega_{\Delta} R_{AB}^6} \left(\int \int (\hat{\mathbf{R}}_{AB} \cdot \mathbf{r}_{A0}) (\hat{\mathbf{R}}_{AB} \cdot \mathbf{r}'_{A0}) \rho_A(\mathbf{r}_A) q_{A,xc}^{(\lambda=1)}(\mathbf{r}'_A | \mathbf{r}_A) d\mathbf{r}_A d\mathbf{r}'_A \right. \\ \left. \times \int \int (\hat{\mathbf{R}}_{AB} \cdot \mathbf{r}_{B0}) (\hat{\mathbf{R}}_{AB} \cdot \mathbf{r}'_{B0}) \rho_B(\mathbf{r}_B) q_{B,xc}^{(\lambda=1)}(\mathbf{r}'_B | \mathbf{r}_B) d\mathbf{r}_B d\mathbf{r}'_B \right) \quad (17)$$

It is clear that this is a R^{-6} attraction. If one defines the dipole moment of the exchange-correlation hole and the reference electron,

$$\mathbf{d}_{A,xc}^{(\lambda=1)}(\mathbf{r}_A) = \int \mathbf{r}'_{A0} q_{A,xc}^{(\lambda=1)}(\mathbf{r}'_A | \mathbf{r}_A) d\mathbf{r}'_A = \int (\mathbf{r}_A - \mathbf{R}_A) q_{A,xc}^{(\lambda=1)}(\mathbf{r}'_A | \mathbf{r}_A) d\mathbf{r}'_A, \quad (18)$$

Eq. 17 can be rewritten as

$$E_{int}^{(2)} \approx \frac{-9\pi}{\omega_{\Delta} R_{AB}^6} \left(\int \rho_A(\mathbf{r}) (\hat{\mathbf{R}}_{AB} \cdot [\mathbf{r} - \mathbf{R}_A]) (\hat{\mathbf{R}}_{AB} \cdot \mathbf{d}_{A,xc}^{(\lambda=1)}(\mathbf{r})) d\mathbf{r} \right. \\ \left. \times \int \rho_B(\mathbf{r}) (\hat{\mathbf{R}}_{AB} \cdot [\mathbf{r} - \mathbf{R}_B]) (\hat{\mathbf{R}}_{AB} \cdot \mathbf{d}_{B,xc}^{(\lambda=1)}(\mathbf{r})) d\mathbf{r} \right) \quad (19)$$

Notice that the dipole moments of the exchange-correlation hole enter into this expression very naturally. This supports the use of the dipole moments of $q_{xc}^{(\lambda=1)}$ in the Becke-Johnson model. By extending the multipole expansion to higher orders, one finds additional contributions from higher-order moments of the $q_{xc}^{(\lambda=1)}$. These dependencies mimic those used by Becke and Johnson for higher-order asymptotic corrections [4,6]. (They, however, simplify their formulas by including only the multipoles that arise from the displacement of $\mathbf{d}_{xc}^{(\lambda=1)}(\mathbf{r})$ away from the atomic center.) The only approximation in Eq. 19 is the neglect of higher-order terms in the multipole expansion.

The approximation in (19) can be written in a slightly simpler form by using a coordinate system based on the center of charge, Eq. 12, and rotating the coordinate system so that \mathbf{R}_{AB} is directed along the z -axis. Then

$$\int \rho_A(\mathbf{r}) (\hat{\mathbf{R}}_{AB} \cdot [\mathbf{r} - \mathbf{R}_A]) (\hat{\mathbf{R}}_{AB} \cdot \mathbf{d}_{A,xc}^{(\lambda=1)}(\mathbf{r})) d\mathbf{r} \\ = \int \rho_A(\mathbf{r}_{A0}) (\hat{\mathbf{R}}_{AB} \cdot [\mathbf{r}_{A0} - \mathbf{R}_A]) (\hat{\mathbf{R}}_{AB} \cdot \mathbf{d}_{A,xc}^{(\lambda=1)}(\mathbf{r}_{A0})) d\mathbf{r}_{A0} \\ = \int \rho_A(\mathbf{r}_{A0}) (r_{A0} \cos(\theta_{A0})) (d_{A,xc}^{(\lambda=1)}(\mathbf{r}_{A0}) \cos(\theta_{d_{A,xc}}(\mathbf{r}_{A0}))) d\mathbf{r}_{A0}, \quad (20)$$

where $d_{A,xc}^{(\lambda=1)}(\mathbf{r}_{A0})$ is the magnitude of the exchange-correlation charge dipole moment and $\theta_{d_{A,xc}}(\mathbf{r}_{A0})$ is the angle between that dipole moment and the z -axis. For a spherically symmetric system the dipole moment is directed against the radial vector

$\left(\mathbf{d}_{A,xc}^{(\lambda=1)}(\mathbf{r}_{A0}) = -\mathbf{r}_{A0}d_{A,xc}^{(\lambda=1)}(\mathbf{r}_{A0})\right)$, and so

$$\begin{aligned} & \int \rho_A(\mathbf{r}) \left(\hat{\mathbf{R}}_{AB} \cdot [\mathbf{r} - \mathbf{R}_A]\right) \left(\hat{\mathbf{R}}_{AB} \cdot \mathbf{d}_{A,xc}^{(\lambda=1)}(\mathbf{r})\right) d\mathbf{r} \\ & \xrightarrow{\text{Spherical system}} - \int \rho_A(r_{A0}) \left(r_{A0}d_{A,xc}^{(\lambda=1)}(\mathbf{r}_{A0})\right) \cos^2(\theta_{A0}) d\mathbf{r}_{A0} \\ & = \frac{-1}{3} \int_0^\infty \rho_A(r_{A0}) r_{A0} d_{A,xc}^{(\lambda=1)}(\mathbf{r}_{A0}) \left(4\pi r_{A0}^2 dr_{A0}\right) \end{aligned} \quad (21)$$

Inserting these forms into Eq. 19 gives produces the results in closest concord with the Becke-Johnson equations in, e.g., Eqs. 13 and 14 of Ref. [2]. The main difference is the instead of containing system averages of $\mathbf{d}_{A,xc}^{(\lambda=1)}(\mathbf{r}_{A0}) \cdot \mathbf{d}_{A,xc}^{(\lambda=1)}(\mathbf{r}_{A0})$, this model employs system averages of $\mathbf{r}_{A0} \cdot \mathbf{d}_{A,xc}^{(\lambda=1)}(\mathbf{r}_{A0})$. Ángyán noted the same disparity, and gives an interesting heuristic argument for why replacing $\left\langle \mathbf{r}_{A0} \cdot \mathbf{d}_{A,xc}^{(\lambda=1)}(\mathbf{r}_{A0}) \right\rangle$ with $\left\langle \mathbf{d}_{A,xc}^{(\lambda=1)}(\mathbf{r}_{A0}) \cdot \mathbf{d}_{A,xc}^{(\lambda=1)}(\mathbf{r}_{A0}) \right\rangle$ might improve results [14].

2.4 Formulas including static polarizability

Unlike Eq. 19, the Becke-Johnson model includes a dependence on both the multipole moments of $q_{xc}^{(\lambda=1)}$ and the polarizability of the interacting systems. This can be achieved by establishing a (necessarily approximate) proportionality between the frequency-dependent linear response and the zero-frequency linear response,

$$\chi_A(\mathbf{r}_A, \mathbf{r}'_A, 0) \underset{\sim}{\propto} \int_0^\infty \chi_A(\mathbf{r}_A, \mathbf{r}'_A, i\omega) d\omega. \quad (22)$$

This relationship is accurate whenever the dominant contribution to the frequency integral in Eq. 22 arises from small values of $i\omega$. This will be most nearly true when the band gap is small, because then the linear response is nearly singular at $i\omega = 0$.

Equation 22 implies that the the linear response and $\rho_A(\mathbf{r}_A) q_{A,xc}^{(\lambda=1)}(\mathbf{r}'_A | \mathbf{r}_A)$ will be approximate proportional, so that

$$\begin{aligned} \alpha_A &= \frac{1}{3} \int \int \mathbf{r}_A \cdot \mathbf{r}'_A \chi_A(\mathbf{r}_A, \mathbf{r}'_A, 0) d\mathbf{r}_A d\mathbf{r}'_A \\ &\underset{\sim}{\propto} \frac{-\pi}{3} \int \int \mathbf{r}_A \cdot \mathbf{r}'_A \rho_A(\mathbf{r}_A) q_{A,xc}^{(\lambda=1)}(\mathbf{r}'_A | \mathbf{r}_A) d\mathbf{r}_A d\mathbf{r}'_A. \end{aligned} \quad (23)$$

We can ensure that this equation is dimensionally consistent by expressing the constant of proportionality as a frequency factor,

$$\alpha_A = \frac{-\pi}{3\omega_\alpha} \int \int \mathbf{r}_A \cdot \mathbf{r}'_A \rho_A(\mathbf{r}_A) q_{A,x_c}^{(\lambda=1)}(\mathbf{r}'_A | \mathbf{r}_A) d\mathbf{r}_A d\mathbf{r}'_A. \quad (24)$$

Using this expression to simplify the approximation to the dispersion interaction in [17] gives

$$E_{\text{int}}^{(2)} = \frac{27\alpha_A}{R_{AB}^6} \left(\frac{\omega_\alpha}{\omega_\Delta} \right) \int \rho_B(\mathbf{r}) \left(\hat{\mathbf{R}}_{AB} \cdot [\mathbf{r} - \mathbf{R}_B] \right) \left(\hat{\mathbf{R}}_{AB} \cdot \mathbf{d}_{B,x_c}^{(\lambda=1)}(\mathbf{r}) \right) d\mathbf{r} \quad (25)$$

This form is acceptable when systems *A* and *B* are chemically identical; in that case Eq. 25 coincides with the formula of Becke and Johnson (compare Eq. 17 in Ref. [2]), except that the system average of $\mathbf{d}_{A,x_c}^{(\lambda=1)}(\mathbf{r}_{A0}) \cdot \mathbf{d}_{A,x_c}^{(\lambda=1)}(\mathbf{r}_{A0})$ (Becke-Johnson) has again been replaced by the system average of $\mathbf{r}_{A0} \cdot \mathbf{d}_{A,x_c}^{(\lambda=1)}(\mathbf{r}_{A0})$ (Ángyán and this work). Note that Eq. 25 is *exact*; the only ambiguity is the (presumably system-dependent) proportionality factors ω_Δ (from Eq. 8) and ω_α (from Eq. 24). These two proportionality factors arise from vaguely similar approximations associating the introduction of (Eq. 8) or removal of (Eqs. 22–24) an integral over the range of imaginary frequencies, and so the ratio $\frac{\omega_\alpha}{\omega_\Delta}$ is probably more nearly equal to a system-independent constant than either factor by itself.

It takes the approximation in Eq. 22/23 literally, and substitutes it into Eq. 9, the Becke-Johnson picture of the dispersion interaction emerges: the exchange-correlation hole charge distribution of one system, $q_{B,x_c}^{(\lambda=1)}(\mathbf{r}'_B | \mathbf{r}_B)$, produces an electric field that induces a “induced dipole response” in the other system. In this model, however, the orientation of $\mathbf{d}_{B,x_c}^{(\lambda=1)}(\mathbf{r})$ and the dipole it induces, $\mathbf{d}_{A,ind}(\mathbf{r})$, relative to the intermolecular coordinate, \mathbf{R}_{AB} , enters into the expression for the interaction energy. The author believes that this dependence is a plausible feature of an accurate dispersion energy model.

2.5 Exchange hole or exchange-correlation hole?

The original Becke-Johnson paper used the dipole moment of the exchange charge, [2]

$$\begin{aligned} q_x(\mathbf{r}' | \mathbf{r}) &= -\rho_x(\mathbf{r}' | \mathbf{r}) - \delta(\mathbf{r} - \mathbf{r}') \\ &= -\frac{|\gamma(\mathbf{r}' | \mathbf{r})|^2}{\rho(\mathbf{r})} - \delta(\mathbf{r} - \mathbf{r}') \\ &= q_{x_c}^{(\lambda=0)}(\mathbf{r}' | \mathbf{r}) \end{aligned} \quad (26)$$

This was subsequently extended to the Becke-Roussel charge, [1, 18] which provides a reasonable approximation to the adiabatic-connection-averaged $q_{xc}^{(\lambda)}(\mathbf{r}'|\mathbf{r})$,

$$q_{xc}^{BR}(\mathbf{r}'|\mathbf{r}) \approx \int_0^1 q_{xc}^{(\lambda)}(\mathbf{r}'|\mathbf{r}) d\lambda. \quad (27)$$

(In fact, because the Becke-Roussel exchange-correlation charge is quite localized, it seems plausible that it provides a good approximation to the qualitative structure of the fully-interacting $q_{xc}^{(\lambda=1)}(\mathbf{r}'|\mathbf{r})$.) Incorporating electron correlation by replacing the exchange-only formulation (using $q_x(\mathbf{r}'|\mathbf{r})$) with the Becke-Roussel model (using $q_{xc}^{BR}(\mathbf{r}'|\mathbf{r})$), does not cause an substantive change in the dispersion energies (and, in fact, seems to slightly improve its accuracy) [1]. This observation supports the use of the fully-interacting exchange-correlation charge in this paper.

It is not that surprising that the incorporating of correlation does not change the Becke-Johnson dispersion model very much. If one decomposes the exchange-correlation charge into its exchange and correlation components,

$$\rho_{xc}^{(\lambda=1)}(\mathbf{r}'|\mathbf{r}) = \rho_x(\mathbf{r}'|\mathbf{r}) + \rho_c(\mathbf{r}'|\mathbf{r}), \quad (28)$$

then the positive charge that “shadows” the position of the electron is represented primarily by the exchange component (which is normalized to -1), rather than the correlation component (which is normalized to zero). So it is plausible that the center-of-charge of $\rho_{xc}^{(\lambda=1)}(\mathbf{r}'|\mathbf{r})$ (which is the dominant factor in determining the dipole moment of $q_{xc}^{(\lambda=1)}(\mathbf{r}'|\mathbf{r})$) is insensitive to correlation effects. To the extent that the correlation is important for determining the multipole moments of $q_{xc}^{(\lambda=1)}$, the dominant effect will be static correlation (which tends to cancel out the long-range tails of $\rho_x(\mathbf{r}'|\mathbf{r})$) and not the dynamical correlation (which has a smaller and more subtle effect on the overall structure of $\rho_{xc}^{(\lambda=1)}(\mathbf{r}'|\mathbf{r})$). The Becke-Roussel functional is a good model of static correlation [19, 20].

3 Discussion

The goal of this paper is to provide some insight into the theoretical foundations of the Becke-Johnson model for the dispersion interaction [1–7]. The first goal is to establish the plausibility of the assumption that underlies the Becke-Johnson model: the dispersion interaction between two well-separated electronic systems may be modeled by considering the interactions between the multipole moments of the exchange(-correlation) holes of the systems. The form of Eqs. 9 and 19 support this picture of the dispersion interaction, although their detailed form is different from that proposed by Becke and Johnson. (These forms, however, are in agreement with the work of Ángyán [14]).

With the plausibility of the Becke-Johnson model established, it becomes interesting to speculate whether the formal analysis in this paper and Ref. [14] can lead to

improvements in Becke-Johnson model. For example, as discussed in II.E, this analysis suggests that the accuracy of the Becke-Johnson model might be improved by replacing the exchange-only electron-hole charge distribution ($q_x(\mathbf{r}'|\mathbf{r}) = q_{xc}^{(\lambda=0)}(\mathbf{r}'|\mathbf{r})$) with the exchange-correlation electron-hole charge distribution, $q_{xc}^{(\lambda=1)}(\mathbf{r}'|\mathbf{r})$. This replacement does not seem to have much effect, but it does support the model based on the Becke-Roussel hole [1].

Recall that by choosing ω_Δ so that the second term in Eq. 9 vanishes, the interaction energy expression takes the simple “electrostatic” form,

$$E_{\text{int}}^{(2)} = \frac{-\pi}{2\omega_\Delta} \int \int \int \int \frac{\rho_A(\mathbf{r}_A) q_{A,xc}^{(\lambda=1)}(\mathbf{r}'_A|\mathbf{r}_A) \rho_B(\mathbf{r}_B) q_{B,xc}^{(\lambda=1)}(\mathbf{r}'_B|\mathbf{r}_B)}{|\mathbf{r}_A - \mathbf{r}_B| |\mathbf{r}'_A - \mathbf{r}'_B|} d\mathbf{r}_A d\mathbf{r}'_A \quad (29)$$

Although this formula tends to Eq. 19 when the subsystems, A and B , are well-separated, it can be evaluated even for subsystems that are close together. Although dispersion-energy expressions based on Eq. 29 would still be “in the spirit” of the Becke-Johnson model, they might not require the use of *ad hoc* damping factors (to eliminate the R^{-6} singularity when the subsystems coincide) or the necessarily arbitrary choice [21, 22] of an atomic partitioning method for the molecular polarizability [15]. It would be reasonable to replace the prefactor ($\frac{-\pi}{2\omega_\Delta}$) in Eq. 29 with an empirical parameter which might be nearly system independent or, failing that, readily approximated by a simple density functional.

Finally, it is interesting that equations similar to those introduced here have been considered in an entirely different area: the nearsightedness of electronic matter [23, 24] and, in particular, the perspective on nearsightedness expounded on by Raffaele Resta [25]. Nearsightedness is also strongly linked to the exchange-correlation hole and its link to the polarization via the fluctuation. I hope that pursuing this link will lead to useful approximations and insights for the as-yet-unknown proportionality factors, ω_Δ (Eq. 8) and ω_α (Eq. 24).

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