## DISPERSION INTERACTION FROM FIRST PRINCIPLES

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We reproduce the classical argument from perturbation theory in quantum mechanics that gives rise to the dispersion $\left(\propto 1 / R^{6}\right)$ interaction between two molecules $A$ and $B$, and obtain the following formula for the energy:

$$
\begin{equation*}
\Delta E^{(2)}=-\frac{3}{\pi R^{6}} \int_{0}^{+\infty} \alpha_{A}(i \omega) \alpha_{B}(i \omega) d \omega \tag{1}
\end{equation*}
$$

where $\alpha_{A}$ and $\alpha_{B}$ are the (spherically-averaged) polarizabilities of each molecule.
Some partial historical landmarks relevant for this document:

- London (1930) applies second-order perturbation theory and proposes the formula

$$
\Delta E^{(2)} \approx-\frac{3}{2} \frac{I_{A} I_{B}}{I_{A}+I_{B}} \frac{\alpha_{A} \alpha_{B}}{R^{6}}
$$

for the energy shift, with $I$ the ionization potential and $\alpha$ the static polarizability

- Casimir and Polder (1948), in the same paper as the one introducing the Casimir-Polder effect, show that including relativistic retardation effects makes the interaction go as $1 / R^{7}$ (although this effect is too weak to be significant in practice)
- McLachlan (1963) simplifies the derivation of Casimir and Polder in the nonrelativistic cases, and introduces the form (1)
- Morgan and Simon (1980) prove rigorously that the $1 / R$ expansion is asymptotic, and that exchange effects are exponentially small
- Tkatchenko and Scheffler (2009) use this theory to add dispersion effects to DFT functionals

Sources:

- The appendix in https://www.lct.jussieu.fr/pagesperso/toulouse/publications/ TouRebGouDobSeaAng-JCP-13.pdf has a nice concise derivation.
- The justification of assuming electrons to be distinguishable ("exponentially small exchange terms") is in Morgan and Simon 1980, https://onlinelibrary.wiley.com/doi/abs/10. 1002/qua. 560170609.
- The IPAM lecture by Alexandre Tkatchenko https://www.youtube.com/watch?v=MXIIGeQ_ Tcg.
These are working notes, not rigorous at all, with liberal use of sloppy notation (same letter for functions and Fourier transforms, delta functions, etc).


## 1. Analogy with statistical mechanics

The usual handwavy explanation for the Van der Waals forces is that quantum fluctuations give rise to instantaneous dipoles, which interact. It is interesting to compare this handwavy argument with the analogous mechanism in statistical mechanics, with quantum fluctuations replaced by the simpler thermal ones (because of the Wick rotation, the hand waving tends to decay more quickly in statistical mechanics than in quantum mechanics).
1.1. The susceptibility. Consider a system with Hamiltonian $H_{0}(q, p)$, with $q, p \in \mathbb{R}^{N}$, and an observable $\mathcal{O}(q, p)$. Typically, we think of a molecule, with $\mathcal{O}$ being the center of mass; a simplistic model is $H_{0}(q, p)=\frac{1}{2}\left(q^{2}+p^{2}\right), \mathcal{O}(q, p)=q$. The Gibbs measure is $d \mu(q, p)=e^{-\beta H_{0}(q, p)} / \int e^{-\beta H_{0}}$. Assume without loss of generality that $\langle\mathcal{O}\rangle_{0}=\int \mathcal{O}(q, p) d \mu(q, p)=0$. Consider now a perturbation of the Hamiltonian $H=H_{0}+\varepsilon \mathcal{P}$. We have

$$
\langle\mathcal{O}\rangle=\frac{\int \mathcal{O} e^{-\beta H}}{\int e^{-\beta H}}
$$

Since

$$
e^{-\beta H} \approx e^{-\beta H_{0}}(1-\beta \varepsilon \mathcal{P})
$$

it follows that

$$
\langle\mathcal{O}\rangle \approx-\beta \varepsilon \frac{\int \mathcal{O} \mathcal{P} e^{-\beta H_{0}}}{\int e^{-\beta H_{0}}}=-\beta \varepsilon\langle\mathcal{O} \mathcal{P}\rangle_{0}
$$

which defines the susceptibility

$$
\chi_{\mathcal{O P}}=-\beta\langle\mathcal{O P}\rangle_{0}
$$

This is a particular case of the (stationary) fluctuation-dissipation theorem: the response to an external perturbation is linked with the fluctuations at equilibrium.
1.2. Two systems in interaction. Consider now two copies of the state space of $H_{0}, A$ and $B$, interacting through the Hamiltonian

$$
H=H_{A}+H_{B}+\varepsilon \mathcal{P}_{A} \mathcal{P}_{B}
$$

where $H_{A}$ and $\mathcal{P}_{A}$ are $H_{0}$ and $\mathcal{P}$ acting on system $A$, and the same for $B$.
The partition function is

$$
\begin{aligned}
Z & =\int e^{-\beta H} \\
& =\int e^{-\beta H_{A}} e^{-\beta H_{B}} \sum_{n} \frac{(-\beta \varepsilon)^{n}}{n!} \mathcal{P}_{A}^{n} \mathcal{P}_{B}^{n} \\
& =Z_{0} \sum_{n} \frac{(-\beta \varepsilon)^{n}}{n!}\left\langle\mathcal{P}_{A}^{n}\right\rangle_{0}\left\langle\mathcal{P}_{B}^{n}\right\rangle_{0} \\
& =Z_{0}\left(1+\beta^{2} \varepsilon^{2}\left\langle\mathcal{P}_{A}^{2}\right\rangle_{0}\left\langle\mathcal{P}_{B}^{2}\right\rangle_{0}+\ldots\right) \\
& =Z_{0}\left(1+\varepsilon^{2} \chi_{\mathcal{P} \mathcal{P}}^{2}+\ldots\right)
\end{aligned}
$$

The two systems decouple at all orders. This means that the partition function (and therefore many quantities, such as the average energy) can be expressed purely in terms of the properties of each system. The calculation gets messy, but simplifies in the case of a harmonic oscillator (it can even be done exactly in that case): the energy shift is proportional to the product of the susceptibilities. Interestingly there does not seem to be a formula analogous to (1) valid for arbitrary systems in the classical case?

## 2. Susceptibility in Quantum mechanics

2.1. Linear response. Let us consider the same system as the one in section 1.1. To simplify matters, we will assume a confined system (with purely discrete spectrum), and will not investigate the convergence of sums, but everything works out even with continuous spectrum. $H_{0}$ is now a many-body Hamiltonian, and $\mathcal{O}$ a possibly many-body observable. $H_{0}$ has spectrum $E_{0}, E_{1}, \ldots$ with eigenstates $\psi_{0}, \psi_{1}, \ldots$ Assume the ground state $\psi_{0}$ is non-degenerate, and that $\langle x\rangle_{0}=$ $\left\langle\psi_{0}, \mathcal{O} \psi_{0}\right\rangle=0$. It will be useful to consider time-dependent perturbations:

$$
i \partial_{t} \psi=H_{0} \psi+\varepsilon f(t) \mathcal{P}, \quad \psi(0)=\psi_{0}
$$

with $f$ causal (zero for negative times). One can apply the (Duhamel/variation of constant) method, and obtain $\psi$ as a (Dyson/Born/time-dependent perturbation theory) series, resulting in

$$
\langle\mathcal{O}(t)\rangle=\langle\psi(t), \mathcal{O} \psi(t)\rangle=\varepsilon \int_{0}^{t} \chi_{\mathcal{O P}}\left(t-t^{\prime}\right) f\left(t^{\prime}\right) d t^{\prime}+O\left(\varepsilon^{2}\right)
$$

where the susceptibility is

$$
\begin{aligned}
\chi_{\mathcal{O P}}(t) & =-i \theta(t)\left\langle\mathcal{O} \psi_{0}, e^{-i\left(H_{0}-E_{0}\right) t} \mathcal{P} \psi_{0}\right\rangle+\text { c.c. } \\
& =-i \theta(t) \sum_{n}\left\langle\psi_{0}, \mathcal{O} \psi_{n}\right\rangle\left\langle\psi_{n}, \mathcal{P} \psi_{0}\right\rangle e^{-i\left(E_{n}-E_{0}\right) t}+\text { c.c. }
\end{aligned}
$$

with $\theta$ the Heaviside function.
Note:

- The addition of the Heaviside function, together with the assumption that $f$ is causal, allows us to take infinite limits in the integral defining $\langle\mathcal{O}(t)\rangle$, and therefore use the convolution theorem.
- This formula is also often written in the interaction picture as $-i\langle[\mathcal{O}(t), \mathcal{P}(0)]\rangle$.
- When $\mathcal{O}$ and $\mathcal{P}$ are one-body multiplication operators by $\delta_{r}$ and $\delta_{r^{\prime}}$, this yields the susceptibility $\chi\left(r, r^{\prime}, t\right)$.
2.2. Fourier transform and imaginary frequencies. Since $\chi$ is causal, we can perform the Fourier transform $\chi(z)=\int \chi(t) e^{i z t} d t$ for any $z$ with $\operatorname{Im}(z)>0$, and obtain

$$
\chi(z)=\sum_{n} \frac{\left\langle\psi_{0}, \mathcal{O} \psi_{n}\right\rangle\left\langle\psi_{n}, \mathcal{P} \psi_{0}\right\rangle}{z-\left(E_{n}-E_{0}\right)}+(\text { c.c. }, z \rightarrow-z) .
$$

In particular, for real orbitals and $\omega>0$,

$$
\begin{aligned}
\chi(i \omega) & =\sum_{n}\left\langle\psi_{0}, \mathcal{O} \psi_{n}\right\rangle\left\langle\psi_{n}, \mathcal{P} \psi_{0}\right\rangle\left(\frac{1}{i \omega-\left(E_{n}-E_{0}\right)}+\frac{1}{-i \omega-\left(E_{n}-E_{0}\right)} .\right) \\
& =\sum_{n}-\frac{2\left(E_{n}-E_{0}\right)\left\langle\psi_{0}, \mathcal{O} \psi_{n}\right\rangle\left\langle\psi_{n}, \mathcal{P} \psi_{0}\right\rangle}{\omega^{2}+\left(E_{n}-E_{0}\right)^{2}}
\end{aligned}
$$

The polarizability $-\chi$ is a positive, decreasing function of $\omega$. A simple example is the harmonic oscillator $H=\frac{1}{2} p^{2}+\frac{1}{2} \omega_{0}^{2} x^{2}$, for which $E_{n}=\frac{1}{2}(n+1)$ and

$$
\langle m| x|n\rangle=\frac{1}{\sqrt{2 \omega}}\langle m| a^{+}+a|n\rangle=\frac{1}{\sqrt{2 \omega}}\left(\delta_{m, n+1} \sqrt{n+1}+\delta_{m, n-1} \sqrt{n}\right)
$$

so that $\langle m, x 0\rangle=\frac{1}{\sqrt{2 \omega}} \delta_{m, 1}$, and

$$
\chi_{x x}(i \omega)=-\frac{1}{\omega^{2}+\omega_{0}^{2}}=-\alpha_{0} \frac{1}{1+\omega^{2} / \omega_{0}^{2}}
$$

with $\alpha_{0}=\frac{1}{\omega_{0}^{2}}$ (this is reasonable: the stiffer an oscillator, the less susceptible it is).

## 3. Weakly interacting systems

We now consider two distinguishable copies $A$ and $B$, with total Hamiltonian, with the same notations as before,

$$
H=H_{A}+H_{B}+\varepsilon \mathcal{P}_{A} \mathcal{P}_{B}
$$

The non-interacting ground state is $\psi_{0}^{A} \otimes \psi_{0}^{B}$, and the states are labelled by $\psi_{n}^{A} \otimes \psi_{m}^{B}$ with energy $E_{n}^{A}+E_{m}^{B}$. From perturbation theory, the first order correction to the ground state is given by

$$
\Delta E^{(1)}=\varepsilon\left\langle\psi_{0}^{A} \otimes \psi_{0}^{B},\left(\mathcal{P}_{A} \mathcal{P}_{B}\right) \psi_{0}^{A} \otimes \psi_{0}^{B}\right\rangle=\varepsilon\left\langle\psi_{0}^{A}, \mathcal{P}_{A} \psi_{0}^{A}\right\rangle\left\langle\psi_{0}^{B}, \mathcal{P}_{B} \psi_{0}^{B}\right\rangle
$$

The second-order term is

$$
\Delta E^{(2)}=-\varepsilon^{2} \sum_{n, m \neq 0} \frac{\left|\left\langle\psi_{0}^{A} \otimes \psi_{0}^{B},\left(\mathcal{P}_{A} \mathcal{P}_{B}\right) \psi_{n}^{A} \otimes \psi_{m}^{B}\right\rangle\right|^{2}}{E_{n}^{A}-E_{0}^{A}+E_{m}^{B}-E_{0}^{B}}=-\varepsilon^{2} \sum_{n, m \neq 0} \frac{\left|\left\langle\psi_{0}^{A}, \mathcal{P}_{A} \psi_{n}^{A}\right\rangle\left\langle\psi_{0}^{B}, \mathcal{P}_{B} \psi_{n}^{B}\right\rangle\right|^{2}}{E_{n}^{A}-E_{0}^{A}+E_{m}^{B}-E_{0}^{B}}
$$

We find that, at variance with the classical case, because of non-commutativity, this does not look easily expressible from the individual properties of each subsystem. However, there is a standard trick to deal with coupling energy denominators. This trick can be performed either in time or frequency domain, and takes the form

$$
\begin{aligned}
\frac{1}{E_{1}+E_{2}} & =\int_{0}^{\infty} e^{-\left(E_{1}+E_{2}\right) t} d t \\
& =\frac{2}{\pi} \int_{0}^{\infty} \frac{E_{1} E_{2}}{\left(E_{1}^{2}+\omega^{2}\right)\left(E_{2}^{2}+\omega^{2}\right)} d \omega
\end{aligned}
$$

for $E_{1}, E_{2}>0$. Note that these two formulas are just Parseval duals of each other, as the transform of $\theta(t) e^{-E t}$ is (proportional to) the Lorentzian $\frac{E}{\omega^{2}+E^{2}}$. Both formulas are of the "imaginary time/frequency" type, since the usual formulas for propagators involve $e^{-i E t}$ and $\frac{1}{\omega-E}$ terms. This trick appears to originate from McLachlan ("Retarded dispersion forces between molecules", 1963), who used it to simplify Casimir and Polder's 1948 treatment of the dispersion forces.

Using this trick, one can decouple the second-order variation as

$$
\begin{aligned}
\Delta E^{(2)}= & -\frac{2}{\pi} \varepsilon^{2} \int_{0}^{+\infty} d \omega\left(\sum_{n \neq 0}\left(E_{n}^{A}-E_{0}^{A}\right) \frac{\left|\left\langle\psi_{0}^{A}, \mathcal{P}^{A} \psi_{n}^{A}\right\rangle\right|^{2}}{\omega^{2}+\left(E_{n}^{A}-E_{0}^{A}\right)^{2}}\right)\left(\sum_{m \neq 0}\left(E_{m}^{B}-E_{0}^{B}\right) \frac{\left|\left\langle\psi_{0}^{B}, \mathcal{P}^{B} \psi_{m}^{B}\right\rangle\right|^{2}}{\omega^{2}+\left(E_{m}^{B}-E_{0}^{B}\right)^{2}}\right) \\
& =-\frac{\varepsilon^{2}}{2 \pi} \int_{0}^{+\infty} \chi_{\mathcal{P} \mathcal{P}}^{A}(i \omega) \chi_{\mathcal{P} \mathcal{P}}^{B}(i \omega) d \omega
\end{aligned}
$$

We now mention another interesting way of obtaining this decoupling, from McLachlan, which has the merit of using marginally less hat-rabbitry:

$$
\sum_{n, m \neq 0} \frac{\left|\left\langle\psi_{0}^{A}, \mathcal{P}_{A} \psi_{n}^{A}\right\rangle\left\langle\psi_{0}^{B}, \mathcal{P}_{B} \psi_{n}^{B}\right\rangle\right|^{2}}{E_{n}^{A}-E_{0}^{A}+E_{m}^{B}-E_{0}^{B}}=\int d E_{1} d E_{2} \frac{f^{A}\left(E_{1}\right) f^{B}\left(E_{2}\right)}{E_{1}+E_{2}}
$$

where

$$
f^{A}(\omega)=\sum_{n}\left|\left\langle\psi_{0}^{A}, \mathcal{P}_{A} \psi_{n}^{A}\right\rangle\right|^{2} \delta\left(\omega-\left(E_{n}^{A}-E_{0}^{A}\right)\right)
$$

and the same for $f^{B}$. This is the spectral measure of the Liouvillian, twice contracted on $\mathcal{P}$. Its significance is that, on $\mathbb{R}^{+}, f^{A}(\omega)=-\frac{1}{\pi} \lim _{\eta \rightarrow 0^{+}} \operatorname{Im} \chi_{\mathcal{P} \mathcal{P}}^{A}(\omega+i \eta)$, and therefore we obtain

$$
\Delta E^{(2)}=\frac{1}{\pi^{2}} \lim _{\eta \rightarrow 0^{+}} \int d E_{1} d E_{2} \frac{\operatorname{Im} \chi_{\mathcal{P} \mathcal{P}}^{A}\left(E_{1}+i \eta\right) \operatorname{Im} \chi_{\mathcal{P} \mathcal{P}}^{B}\left(E_{2}+i \eta\right)}{E_{1}+E_{2}}
$$

which relates the energy variation to the susceptibility. This now becomes "just" an exercice in complex function theory, and using the various evenness properties, the Kramers-Kronig relations and contour deformation then yields the result.

Finally, note that when the perturbation is instead $\varepsilon \sum_{i} \mathcal{P}_{i}^{A} \mathcal{P}_{i}^{B}$, the result is

$$
\Delta E^{(2)}=-\frac{\varepsilon^{2}}{2 \pi} \sum_{i, j} \int_{0}^{+\infty} \chi_{i j}^{A}(i \omega) \chi_{j i}^{B}(i \omega) d \omega
$$

## 4. Application to Van der Waals systems

Consider two molecules $A$ and $B$, with internal Hamiltonians $H_{A}, H_{B}$, and put them in contact with Hamiltonian $H$. Formulating this as a problem of the previous form is tricky because of the indistinguishably of the electrons, which makes it hard to apply perturbation theory. It is true that if $E$ is an eigenvalue of $H$ with symmetry constraints, then $E$ is also an eigenvalue of $H$ without symmetry constraints, and one can apply perturbation theory without care for symmetry. There is however complications. First, symmetry-unconstrained eigenstates of $H_{A} \otimes 1+1 \otimes H_{B}$ are not isolated. Second, for more than two electrons, the (symmetry-constrained) ground state might lie inside the continuous spectrum of the symmetry-unconstrained operator. This is the case already for non-interacting hydrogen with three electrons, where the (unphysical) symmetry-unconstrained continuous spectrum starts at $2 E_{0}$, which might be below the actual ground state $E_{0}+E_{1}+E_{2}$. Perturbation theory for eigenvalues embedded inside continuous spectrum is more involved, and generally creates resonances. Third, complication is that the ground state of the molecular problem is not necessarily $A+B$ but may be $A^{+}+B^{-}$or other ions.

A possible alternative is to embrace antisymmetry and write the perturbation expansion in terms of the eigenstates of the symmetry-constrained eigenstates (eg $\left.\frac{1}{\sqrt{2}}\left(\phi_{n}^{A}\left(r_{1}\right) \phi_{m}^{B}\left(r_{2}\right)-\phi_{m}^{B}\left(r_{1}\right) \phi_{n}^{A}\left(r_{2}\right)\right)\right)$ and to argue that the cross-terms (overlap terms) in the matrix elements are small because the eigenstates of each system do not overlap on the other. This is plausible for low-lying bound states, but wrong for continuum scattering eigenstates.

We refer to Morgan and Simon 1980, https://onlinelibrary.wiley.com/doi/abs/10.1002/ qua. 560170609 for a proof that it works out in the end, but we do not discuss this further and assume distinguishability (ie that we are considering $H$ on the space of wavefunctions that satisfy antisymmetry only among the intra-molecular electrons). Then, we can write the interacting Hamiltonian as

$$
H_{A B}=\sum_{i \in A, j \in B} \frac{z_{i} z_{j}}{\left|r_{i}-r_{j}\right|}
$$

where the sum runs over all particles, both electrons and nuclei, even when the nuclei are classical (this is convenient to avoid separating them in the electrostatics. In fact, the whole theory works exactly the same if one assumes quantum nuclei).

This perturbing Hamiltonian is not in the sum-of-product-of-observables form needed to apply the above result. However, one can write

$$
H_{A B}=\int d r_{A} d r_{B} n_{A}\left(r_{A}\right) n_{B}\left(r_{B}\right) \frac{1}{\left|r_{A}-r_{B}\right|}
$$

where we define the charge density operators by the relationship that $\left\langle\psi, n_{I}(r) \psi\right\rangle=\rho_{I}(r)$, the total (electron and nuclei) charge density of the particles of system $I$ at point $r$. The first-order variation is easily seen to be

$$
\Delta E^{(1)}=\int d r_{A} d r_{B} \frac{\rho_{A}\left(r_{A}\right) \rho_{B}\left(r_{B}\right)}{\left|r_{A}-r_{B}\right|}
$$

the usual electrostatic interaction which can be computed by multipole expansion.
The second-order variation is obtained by using the result of the previous section with the perturbing hamiltonian $H_{A B}$ above; the result is

$$
\begin{equation*}
\Delta E^{(2)}=-\frac{1}{2 \pi} \int_{0}^{+\infty} \int \frac{\chi^{A}\left(r_{A}, r_{A}^{\prime}, i \omega\right) \chi^{B}\left(r_{B}, r_{B}^{\prime}, i \omega\right)}{\left|r_{B}-r_{A}\right|\left|r_{B}^{\prime}-r_{A}^{\prime}\right|} d \omega d r_{A} d r_{B} d r_{A}^{\prime} d r_{B}^{\prime} \tag{2}
\end{equation*}
$$

We now plug the multipole expansion around arbitrarily chosen centers $r_{A}^{0}, r_{B}^{0}$

$$
\begin{equation*}
\frac{1}{\left|r_{A}-r_{B}\right|}=\frac{1}{\left|r_{A}^{0}-r_{B}^{0}\right|}-\sum_{i=1}^{3} \frac{r_{A i}^{0}-r_{B i}^{0}}{\left|r_{A}-r_{B}\right|^{3}}\left(\left(r_{B}-r_{B}^{0}\right)-\left(r_{A}-r_{A}^{0}\right)\right)+\ldots \tag{3}
\end{equation*}
$$

Since the integral of $\chi$ over either its first or second argument vanishes (constant charge, and zero response to constant perturbation), the leading term is

$$
\Delta E^{(2)}=-\frac{3}{\pi\left|r_{A}^{0}-r_{B}^{0}\right|^{6}} \int_{0}^{+\infty} \alpha_{A}(i \omega) \alpha_{B}(i \omega) d \omega
$$

where

$$
\alpha_{I}(i \omega)=-\frac{1}{3} \sum_{i} \chi_{\left(r_{A i}\right),\left(r_{A i}\right)}^{I}
$$

is the spherically averaged polarizability (response of dipole moment to external field); note that $r_{A / B}^{0}$ plays no role because of charge neutrality.

Note finally that assuming the harmonic oscillator ansatz $\alpha(i \omega)=\alpha_{0} \frac{\omega_{0}^{2}}{\omega^{2}+\omega_{0}^{2}}$ and taking $\omega_{0}$ to be the ionization energy, we obtain the classical London (1930) dispersion energy

$$
\Delta E^{(2)} \approx-\frac{3}{2} \frac{I_{A} I_{B}}{I_{A}+I_{B}} \frac{\alpha_{A} \alpha_{B}}{R^{6}}
$$

## 5. Homogenization of susceptibilities

We note here an alternative way of deriving the multipole expansion, approximating the susceptibilities rather than the interaction as we did in (3). Consider a susceptibility kernel $\chi$ (mapping variations in potential to variations in density), and ask the question: what does it look like at large scales? That is, what is

$$
\int u(r) K\left(r, r^{\prime}\right) v\left(r^{\prime}\right) d r d r^{\prime}
$$

when $K$ is localized to a region of space (centered at $(0,0))$ and $u, v$ are large scale. Mathematically, the question is: what is the asymptotic expansion in the sense of distributions of $K\left(r / \varepsilon, r^{\prime} / \varepsilon\right)$. We perform the computation in 1D for simplicity. Taylor expanding $u$ and $v$ at 0 , we get, with $K_{n m}=\int r^{n} r^{m} K\left(r, r^{\prime}\right) d r d r^{\prime}$,

$$
\int u(r) K\left(r, r^{\prime}\right) v\left(r^{\prime}\right) d r d r^{\prime}=u(0) v(0) K_{00}+u^{\prime}(0) v(0) K_{10}+u(0) v^{\prime}(0) K_{01}+u^{\prime}(0) v^{\prime}(0) K_{11}+\ldots
$$

so in the sense of distributions,

$$
\chi\left(r, r^{\prime}\right) \approx \delta(r) \delta\left(r^{\prime}\right) K_{00}-\delta(r) \delta\left(r^{\prime}\right) K_{10}+\delta^{\prime}(r) \delta\left(r^{\prime}\right) K_{01}+\delta^{\prime}(r) \delta^{\prime}\left(r^{\prime}\right) K_{11}+\ldots
$$

Plugging this result in (2) yields the result.

