

Quantum mechanical approaches to the virial

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In this note, we approach the virial from a standard quantum mechanics point of view. Section 1 reviews the classical virial theorem. Section 2 reviews the Ehrenfest theorem as we will use it in the quantum discussion. Then the virial is considered quantum mechanically in two different ways. In section 3, the expectation values of the position and momentum observables considered independently are used to construct a "classical" virial for which we derive the virial theorem and thereby establish a property of wave function. In section 4, we define a quantum virial observable and establish the quantum virial theorem. Section 5 is a brief discussion and conclusion highlighting the fact the quantum virial theorem is in direct correspondence with the classical virial theorem while the "classical" virial considered from a quantum mechanical approach merely corresponds to an integral property of the wave functions.

I. VIRIAL THEOREM IN CLASSICAL MECHANICS

The virial is a quantity that arises from considering the time derivative of the moment of inertia I about the origin for a system of particles. Take a system of N particles, each with a mass m_i , position \mathbf{r}_i and momentum \mathbf{p}_i with i running from 1 to N . Then $I = \sum_{i=1}^N m_i |\mathbf{r}_i|^2$ and

$$\frac{dI}{dt} = \sum_{i=1}^N 2m_i \mathbf{r}_i \cdot \frac{d\mathbf{r}_i}{dt} = 2 \sum_{i=1}^N \mathbf{r}_i \cdot \mathbf{p}_i = 2G$$

where $G = \sum_{i=1}^N \mathbf{r}_i \cdot \mathbf{p}_i$ defines the virial.

We can then look at the time derivative of the virial:

$$\frac{dG}{dt} = \sum_{i=1}^N \frac{d\mathbf{r}_i}{dt} \cdot \mathbf{p}_i + \sum_{i=1}^N \mathbf{r}_i \cdot \frac{d\mathbf{p}_i}{dt} = 2T + \sum_{i=1}^N \mathbf{r}_i \cdot \mathbf{F}_i$$

where we introduced T the kinetic energy of the entire system and the force \mathbf{F}_i acting on the i^{th} particle .

The virial theorem derives from considering the time average of the time derivative of the virial. We denote the average over a time period τ as $\overline{(\dots)}_\tau$.

In a reference frame where the the system is globally at rest, $\sum_{i=1}^N \mathbf{p}_i = 0$, a finite and stable bound system would be such that \mathbf{r}_i and \mathbf{p}_i are bound, so, in the limit of infinite times, the time average $\overline{\left(\frac{dG}{dt}\right)}_\infty = 0$. Consequently,

$$2\overline{(T)}_\infty = -\overline{\left(\sum_{i=1}^N \mathbf{r}_i \cdot \mathbf{F}_i\right)}_\infty \quad (1)$$

which express the virial theorem [5] in its general form.

We may then consider each particle to only be under the influence of a superposition of pairwise interactions with every other particle. The force exerted by all the particles of the system on the i^{th} particle is $\mathbf{F}_i = \sum_{j=1; j \neq i}^N \mathbf{F}_{ij}$ where \mathbf{F}_{ij} is the force exerted by particle j on particle i . With this, we can write

$$\sum_{i=1}^N \mathbf{r}_i \cdot \mathbf{F}_i = \sum_{i=1}^N \sum_{j < i} \mathbf{r}_i \cdot \mathbf{F}_{ij} + \sum_{i=1}^N \sum_{j > i} \mathbf{r}_i \cdot \mathbf{F}_{ij} = \sum_{i=1}^N \sum_{j < i} (\mathbf{r}_i - \mathbf{r}_j) \cdot \mathbf{F}_{ij} \quad (2)$$

where we used [6] the fact that $\mathbf{F}_{ij} = -\mathbf{F}_{ji}$.

We now further restrict ourselves to the cases in which the force between any two particles derives from a central potential $V(|r|)$:

$$\mathbf{F}_{ij} = -\nabla_i V(|\mathbf{r}_i - \mathbf{r}_j|) = -\frac{dV}{dr} \frac{\mathbf{r}_i - \mathbf{r}_j}{|\mathbf{r}_i - \mathbf{r}_j|} = -\frac{dV}{dr} \frac{\mathbf{r}_i - \mathbf{r}_j}{r_{ij}}$$

Using this in the above result, we obtain: $\sum_{i=1}^N \mathbf{r}_i \cdot \mathbf{F}_i = -\sum_{i=1}^N \sum_{j<i} r_{ij} \frac{dV}{dr}$. So we have, for the virial theorem, the form:

$$2\overline{(T)}_\infty = \overline{\left(\sum_{i=1}^N \sum_{j<i} r_{ij} \frac{dV}{dr}(r_{ij}) \right)}.$$

Furthermore, if the interaction potential energy is proportional to a power law of the distance $V(r) = V_0 \cdot r^\nu$, then, introducing the total potential energy of the system $V_{Tot} = \sum_{i=1}^N \sum_{j<i} V(r_{ij})$, the virial theorem takes its most usual form:

$$2\overline{(T)}_\infty = \nu \overline{(V_{Tot})}_\infty \quad (3)$$

This can be applied with $\nu = -1$ in the case of a Keplerian potential or with $\nu = 2$ in the case of a network of harmonic oscillators.

II. THE EHRENFEST THEOREM

The virial theorem discussed in the previous section concerns time averaging $\overline{(\dots)}_\infty$ in the limit of infinite times. In the quantum discussion of the properties of the virial, this need to be combined with the statistical nature of the outcome of measurements in quantum mechanics. As a consequence, we are going to concentrate on the time evolution of expectation values. Considering an observable A , the expectation value of this observable is denoted $\langle A \rangle = \langle \phi(t) | A | \phi(t) \rangle$ when the considered system is in the quantum state $|\phi(t)\rangle$. The Ehrenfest theorem provides an expression for the time derivative of expectation values. In order to establish this expression, we can proceed directly from the definition of $\langle A \rangle$:

$$\frac{d}{dt} \langle A \rangle = \left(\frac{d}{dt} \langle \phi(t) | \right) A | \phi(t) \rangle + \langle \phi(t) | A \left(\frac{d}{dt} | \phi(t) \rangle \right) + \langle \phi(t) | \frac{\partial A}{\partial t} | \phi(t) \rangle$$

We assumed A includes an explicit time dependence. If the time evolution of the state of the system is governed by the Schrödinger equation with a Hamiltonian H , then, $i\hbar \frac{d}{dt} |\phi\rangle = H |\phi\rangle$ and, since H is hermitian, $i\hbar \frac{d}{dt} \langle \phi| = -\langle \phi| H$. So we obtain the expression of the Ehrenfest theorem:

$$\frac{d}{dt} \langle A \rangle = \frac{1}{i\hbar} \langle \phi(t) | AH - HA | \phi(t) \rangle + \langle \phi(t) | \frac{\partial A}{\partial t} | \phi(t) \rangle$$

or, using the usual notations for the commutator and the expectation value,

$$\frac{d}{dt} \langle A \rangle = \frac{1}{i\hbar} \langle [A, H] \rangle + \left\langle \frac{\partial A}{\partial t} \right\rangle$$

Particularly interesting applications of the Ehrenfest theorem appear when considering position $A = R$ and momentum $A = P$ operators. Consider a particle of mass m whose evolution is governed by a Hamiltonian $H = P^2/2m + V$ where V is the potential energy. In order to apply the Ehrenfest theorem, we need to express the commutator $[R, H]$ and $[P, H]$. This can be done using $[R, P] = i\hbar$:

$$\begin{aligned} [R, H] &= \frac{1}{2m} [R, P^2] = \frac{1}{2m} (RP^2 - P^2R) \\ &= \frac{1}{2m} ((i\hbar + PR)P - P(RP - i\hbar)) = i\hbar \frac{P}{m} \end{aligned}$$

We also need to express $[P, H] = [P, V]$, which can be done in position representation with $P = \frac{\hbar}{i} \frac{\partial}{\partial R} = \frac{\hbar}{i} \nabla$:

$$[P, H] = [P, V] = \frac{\hbar}{i} (\nabla V - V \nabla) = \frac{\hbar}{i} ((\nabla V) + V \nabla - V \nabla) = \frac{\hbar}{i} (\nabla V)$$

Since R and P do not have any explicit time dependence, the Ehrenfest theorem then directly gives the two following relations for the i^{th} particle of the quantum analog of the classical system considered in our discussion of the virial theorem in section I:

$$\frac{d}{dt}\langle\mathbf{R}_i\rangle = \langle\frac{\mathbf{P}_i}{m}\rangle \quad (4)$$

$$\frac{d}{dt}\langle\mathbf{P}_i\rangle = -\langle\nabla_i V_{Tot}\rangle = \langle\mathbf{F}_i\rangle \quad (5)$$

These are Hamilton's equations in which we re-introduced \mathbf{F}_i , the force acting on particle i . The time derivative of the expected values of the positions are equal to the expectation values of momenta divided by the mass. The time derivatives of the expectation values momenta are equal to the expectation values of the forces. This is an important result as it provides a bridge between the quantum and classical regimes. It establishes that the time evolution of expectation values in Born's probabilistic interpretation of quantum mechanics matches the prescriptions of classical mechanics.

III. CLASSICAL VIRIAL THEOREM IN THE QUANTUM REGIME

The state of a system of N distinguishable particles can be described by the direct product of the wave functions of its individual constituents. We can then *classically* define the virial as $G_C = \sum_{i=1}^N \langle\mathbf{P}_i\rangle\langle\mathbf{R}_i\rangle$ with \mathbf{R}_i and \mathbf{P}_i the position and momentum operators for particle i . This virial can be regarded as *classical* since, following the Ehrenfest theorem, $\langle\mathbf{R}_i\rangle$ and $\langle\mathbf{P}_i\rangle$ in the quantum system will evolve with time in exactly the same way as \mathbf{r}_i and \mathbf{p}_i in the classical system for which we have established the virial theorem in Section I. In particular, we already know that the classical virial theorem (Equation 1) directly applies:

$$\overline{\left(\sum_{i=1}^N \frac{\langle\mathbf{P}_i\rangle^2}{m_i}\right)}_{\infty} = \overline{\left(\sum_{i=1}^N \langle\mathbf{R}_i\rangle \cdot \langle\mathbf{F}_i\rangle\right)}_{\infty} = \overline{\left(\sum_{i=1}^N \sum_{j<i} (\langle\mathbf{R}_i\rangle - \langle\mathbf{R}_j\rangle) \cdot \langle\mathbf{F}_{ij}\rangle\right)}_{\infty}$$

If the force \mathbf{F}_{ij} derives from a central potential of the form $V_0|\mathbf{R}_i - \mathbf{R}_j|^\nu$, this gives.

$$\overline{\left(\sum_{i=1}^N \frac{\langle\mathbf{P}_i\rangle^2}{m_i}\right)}_{\infty} = \nu V_0 \overline{\left(\sum_{i=1}^N \sum_{j<i} (\langle\mathbf{R}_i\rangle - \langle\mathbf{R}_j\rangle) \cdot \langle|\mathbf{R}_i - \mathbf{R}_j|^{\nu-2}(\mathbf{R}_i - \mathbf{R}_j)\rangle\right)}_{\infty} \quad (6)$$

But still, let us follow the derivation as an exercise. Noting the components $k \in \{x, y, z\}$ of the position and momentum of the i^{th} particle as R_i^k and P_i^k respectively, we can take the time derivative of G_C :

$$\frac{d}{dt}G_C = \sum_{i=1}^N \sum_k \left(\left(\frac{d}{dt}\langle P_i^k \rangle \right) \langle R_i^k \rangle + \langle P_i^k \rangle \left(\frac{d}{dt}\langle R_i^k \rangle \right) \right)$$

We can then apply the Ehrenfest theorem:

$$\frac{d}{dt}G_C = \frac{1}{i\hbar} \sum_{i=1}^N \sum_k (\langle [P_i^k, H] \rangle \langle R_i^k \rangle + \langle P_i^k \rangle \langle [R_i^k, H] \rangle)$$

And, using the expressions we found for the commutators $[R, H]$ and $[P, H]$ in Section II

$$\frac{dG_C}{dt} = -\sum_{i=1}^N \sum_k \langle R_i^k \rangle \langle \frac{\partial V_{Tot}}{\partial R_i^k} \rangle + \sum_{i=1}^N \frac{\langle \mathbf{P}_i \rangle^2}{m_i}$$

Where we make use of the total potential energy operator,

$$V_{Tot} = \sum_{l=1}^N \sum_{j<l} V(|\mathbf{R}_l - \mathbf{R}_j|) = \frac{1}{2} \sum_{l=1}^N \sum_{j \neq l} V(|\mathbf{R}_l - \mathbf{R}_j|)$$

and in the case of the power law central potential:

$$\frac{\partial V_{Tot}}{\partial R_i^k} = \nu V_0 \sum_{j \neq i} |\mathbf{R}_i - \mathbf{R}_j|^{\nu-2} (R_i^k - R_j^k)$$

Time averaging for a bound system in the reference frame where it is at rest $\overline{\left(\frac{dG_Q}{dt}\right)}_\infty = 0$, we obtain

$$\overline{\left(\sum_{i=1}^N \frac{\langle \mathbf{P}_i \rangle^2}{m_i}\right)}_\infty = \nu V_0 \overline{\left(\sum_{i=1}^N \sum_{j \neq i} \sum_k \langle R_i^k \rangle \langle |\mathbf{R}_i - \mathbf{R}_j|^{\nu-2} (R_i^k - R_j^k) \rangle\right)}_\infty \quad (7)$$

Using the same manipulation as in Section I (see Equation 2), we find this is equivalent to Equation 8 and we have completed a quantum mechanical derivation of the classical virial theorem.

$$\overline{\left(\sum_{i=1}^N \frac{\langle \mathbf{P}_i \rangle^2}{m_i}\right)}_\infty = \nu V_0 \overline{\left(\sum_{i=1}^N \sum_{j < i} (\langle \mathbf{R}_i \rangle - \langle \mathbf{R}_j \rangle) \cdot \langle |\mathbf{R}_i - \mathbf{R}_j|^{\nu-2} (\mathbf{R}_i - \mathbf{R}_j) \rangle\right)}_\infty \quad (8)$$

It should be noted that the lefthand side is not the time averaged expectation value of the kinetic energy. It is the time averaged kinetic energy for the expectation value of the momenta. In the same way, the right hand side can not be written simply in terms of the total potential energy so the classical virial theorem can not be expressed quantum-mechanically in a form similar to Equation 3.

In this equation, it should be highlighted that the expectation values $\langle \dots \rangle$ are to be understood as calculated for the many particle quantum state $|\phi(t)\rangle$ of the system in the course of its evolution following Schrödinger's equation. This quantum form of the classical virial theorem therefore stands as a non-trivial property of the solution of the Schrödinger equation.

IV. QUANTUM VIRIAL THEOREM

We could also consider the expectation value of the quantum virial $G_Q = \sum_{i=1}^N \sum_k \langle P_i^k \cdot R_i^k \rangle$. This is the usual approach to the virial theorem in quantum mechanics as originally investigated by Vladimir Fock [3] in 1930. Alternatively, we could consider $G_Q^\dagger = \sum_{i=1}^N \sum_k \langle R_i^k \cdot P_i^k \rangle$. However, as long as we are interested only in the time derivative of the expectation value of G_Q (or G_Q^\dagger), this makes no difference. Indeed:

$$\frac{dG_Q}{dt} = \frac{d}{dt} \sum_{i=1}^N \sum_k \langle P_i^k R_i^k \rangle = \frac{d}{dt} \sum_{i=1}^N \sum_k (\langle R_i^k \cdot P_i^k \rangle - i\hbar) = \frac{dG_Q^\dagger}{dt}$$

Since there are no explicit time dependences, the Ehrenfest theorem gives:

$$\frac{dG_Q}{dt} = \frac{1}{i\hbar} \sum_{i=1}^N \sum_k \langle [P_i^k \cdot R_i^k, H] \rangle$$

Considering the same Hamiltonian as in the previous section, we see that we need to calculate $[G_Q, P^2]$

$$[P_i^k R_i^k, P_i^{k2}] = P_i^k R_i^k P_i^{k2} - P_i^{k3} R_i^k = P_i^k (R_i^k P_i^{k2} - P_i^{k2} R_i^k) = 2i\hbar P_i^{k2}$$

and $[G_Q, V]$ can be obtained in position representation:

$$\begin{aligned} [P_i^k R_i^k, V_{Tot}] &= \frac{\hbar}{i} \left(\frac{\partial}{\partial R_i^k} R_i^k V_{Tot} - V_{Tot} \frac{\partial}{\partial R_i^k} R_i^k \right) \\ &= \frac{\hbar}{i} \left(V_{Tot} + R_i^k \left(\frac{\partial V}{\partial R_i^k} \right) + R_i^k V_{Tot} \frac{\partial}{\partial R_i^k} - V_{Tot} - V_{Tot} R_i^k \frac{\partial}{\partial R_i^k} \right) \\ &= \frac{\hbar}{i} R_i^k \cdot \frac{\partial V}{\partial R_i^k} \end{aligned}$$

so

$$[P_i^k R_i^k, H] = i\hbar \frac{P_i^{k2}}{m_i} - i\hbar R_i^k \frac{\partial V_{Tot}}{\partial R_i^k}$$

with this:

$$\frac{dG_Q}{dt} = \sum_{i=1}^N \sum_k \frac{\langle P_i^{k2} \rangle}{m_i} - \sum_{i=1}^N \sum_k \langle R_i^k \frac{\partial V_{Tot}}{\partial R_i^k} \rangle$$

Here we recognize the first term as twice the expectation value of the system kinetic energy $T = \sum_{i=1}^N \sum_k \frac{\langle P_i^{k2} \rangle}{2m_i}$. At the same time, considering the time average over an infinite period, a bound system in its rest frame satisfies $\overline{\left(\frac{dG_Q}{dt}\right)}_\infty = 0$

so that $2\overline{(T)}_\infty = \overline{\left(\sum_{i=1}^N \sum_k \langle R_i^k \frac{\partial V_{Tot}}{\partial R_i^k} \rangle\right)}_\infty$.

In cases where the potential energy is a power law of index ν :

$$2\overline{(T)}_\infty = \overline{\left(\nu \sum_{i=1}^N \sum_{j \neq i} \sum_k \langle R_i^k \frac{V(|\mathbf{R}_i - \mathbf{R}_j|)}{|\mathbf{R}_i - \mathbf{R}_j|} \frac{R_i^k - R_j^k}{|\mathbf{R}_i - \mathbf{R}_j|} \rangle\right)}_\infty$$

or

$$2\overline{(T)}_\infty = \overline{\left(\nu \sum_{i=1}^N \sum_{j \neq i} \langle \frac{V(|\mathbf{R}_i - \mathbf{R}_j|)}{|\mathbf{R}_i - \mathbf{R}_j|} \frac{|\mathbf{R}_i|^2 - \mathbf{R}_i \cdot \mathbf{R}_j}{|\mathbf{R}_i - \mathbf{R}_j|} \rangle\right)}_\infty$$

or

$$2\overline{(T)}_\infty = \overline{\left(\nu \sum_{i=1}^N \sum_{j < i} \langle \frac{V(|\mathbf{R}_i - \mathbf{R}_j|)}{|\mathbf{R}_i - \mathbf{R}_j|} \frac{|\mathbf{R}_i|^2 - 2\mathbf{R}_i \cdot \mathbf{R}_j + |\mathbf{R}_j|^2}{|\mathbf{R}_i - \mathbf{R}_j|} \rangle\right)}_\infty$$

or

$$2\overline{(T)}_\infty = \overline{\left(\nu \sum_{i=1}^N \sum_{j < i} \langle V(|\mathbf{R}_i - \mathbf{R}_j|) \rangle\right)}_\infty$$

or, finally,

$$2\overline{(T)}_\infty = \nu \overline{\langle V_{Tot} \rangle}_\infty$$

and we recover the virial theorem in the exact same formulation as in classical mechanics except for the fact that the kinetic and potential energies have to be replaced by their expectation values.

V. SUMMARY AND CONCLUSIONS

We have defined the virial for a quantum system in two different ways.

In Section III, we considered a *classical* virial, $G_C = \sum_{i=1}^N \langle \mathbf{P}_i \rangle \langle \mathbf{R}_i \rangle$. Since $\langle \mathbf{P}_i \rangle$ and $\langle \mathbf{R}_i \rangle$ have the same equation of motion as the corresponding quantities in the classical system, we could apply the classical virial theorem directly to the quantum form replacing \mathbf{r}_i , \mathbf{p}_i and \mathbf{F}_i by their expectation values. We were then able to derive the same relation quantum-mechanically:

$$\overline{\left(\sum_{i=1}^N \frac{\langle \mathbf{P}_i \rangle^2}{m_i}\right)}_\infty = \nu V_0 \overline{\left(\sum_{i=1}^N \sum_{j < i} (\langle \mathbf{R}_i \rangle - \langle \mathbf{R}_j \rangle) \cdot \langle |\mathbf{R}_i - \mathbf{R}_j|^{\nu-2} (\mathbf{R}_i - \mathbf{R}_j) \rangle\right)}_\infty$$

The classical virial theorem can be seen as an integral property of the solutions of the Schrödinger equation.

In Section IV, we considered the more usual *quantum* virial, $G_Q = \sum_{i=1}^N \langle \mathbf{P}_i \cdot \mathbf{R}_i \rangle$. We obtained a virial theorem with exactly the same form as in classical mechanics provided the kinetic and potential energies are replaced by their quantum mechanical expectation values:

$$2\overline{\langle T \rangle}_\infty = \nu \overline{\langle V_{Tot} \rangle}_\infty$$

This suggests that the operation of taking the expectation value $\langle \dots \rangle$ can be regarded as a continuation of the time averaging $\overline{(\dots)}_\tau$ to reveal the contribution of a dynamics internal to the wave function. In fact, when considering the system to be in a stationary state, the time averaging becomes superfluous and we obtain a relation between expectation values $2\langle T \rangle = \nu \langle V_{Tot} \rangle$ which, when regarded as the time averaging of an internal dynamics, is identical to the classical form of the virial theorem: $2\overline{\langle T \rangle}_\infty = \nu \overline{\langle V_{Tot} \rangle}_\infty$. At the same time and in complementarity, the virial theorem for G_C becomes degenerate since there are no dynamics other than those *internal* to the wave function, leading to $\langle \mathbf{P}_i \rangle = 0$.

This consideration of the virial theorem in quantum mechanics certainly does not provide any proof for the necessity of an explicit continuation between the classical dynamic dominating at scales larger than the de Broglie wavelength and a particulate dynamic *internal* to the wave function. However, the fact that the classical (Section I) and quantum (Section IV) virial theorems are identical in form, follows well from Nelson's stochastic quantization [2] and more recently from Nottale's scale relativity [4]. From these point of views, the wave function property revealed by the quantum consideration of the classical virial in Section III can be seen as a superfluous matching constraint appearing because of the artificial discrimination between the dynamics at classical and quantum scales, with the wave function merely playing the role of a wrapper of the latter.

VI. ACKNOWLEDGEMENT

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 - [2] E.Nelson, "Derivation of the Schrödinger Equation from Newtonian Mechanics", Phys. Rev. 150, 1079 (1966)
 - [3] V.Fock, "Bemerkung zum Virialsatz". Zeitschrift für Physik A **63** (11): 855858 (1930)
 - [4] L.Nottale, "Scale Relativity And Fractal Space-Time: A New Approach to Unifying Relativity and Quantum Mechanics"; World Scientific Publishing Company; 1 edition, 2011; ISBN 978-1848166509
 - [5] The word "virial" derives from latin "vis" which mean force. The word and the theorem are both due to Rudolf Clausius in 1870 in "On a Mechanical Theorem Applicable to Heat", in Philosophical Magazine, Ser. 4, vol. 40, 1870, p. 122127
 - [6] Using the fact that $\mathbf{F}_{ij} = -\mathbf{F}_{ji}$, we have:

$$\sum_{i=1}^N \mathbf{r}_i \cdot \mathbf{F}_i = \sum_{i=1}^N \sum_{j<i} \mathbf{r}_i \cdot \mathbf{F}_{ij} + \sum_{i=1}^N \sum_{j>i} \mathbf{r}_i \cdot \mathbf{F}_{ij} = \sum_{i=1}^N \sum_{j<i} \mathbf{r}_i \cdot \mathbf{F}_{ij} - \sum_{i=1}^N \sum_{j>i} \mathbf{r}_i \cdot \mathbf{F}_{ji}$$

We can write the last term regrouping those obtained for the same values of j :

$$\sum_{i=1}^N \sum_{j>i} \mathbf{r}_i \cdot \mathbf{F}_{ji} = (\mathbf{r}_1 \cdot \mathbf{F}_{21}) + (\mathbf{r}_1 \cdot \mathbf{F}_{31} + \mathbf{r}_2 \cdot \mathbf{F}_{32}) + (\mathbf{r}_1 \cdot \mathbf{F}_{41} + \mathbf{r}_2 \cdot \mathbf{F}_{42} + \mathbf{r}_3 \cdot \mathbf{F}_{43}) + \dots$$

and we see that

$$\sum_{i=1}^N \sum_{j>i} \mathbf{r}_i \cdot \mathbf{F}_{ji} = \sum_{j=1}^N \sum_{i<j} \mathbf{r}_i \cdot \mathbf{F}_{ji} = \sum_{i=1}^N \sum_{j<i} \mathbf{r}_j \cdot \mathbf{F}_{ij}$$

Combining the two terms in the original expression:

$$\sum_{i=1}^N \mathbf{r}_i \cdot \mathbf{F}_i = \sum_{i=1}^N \sum_{j<i} (\mathbf{r}_i - \mathbf{r}_j) \cdot \mathbf{F}_{ij}$$