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UPPER LIMITS ON THE ROSSELAND MEAN OPACITY

by

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ABSTRACT

Using sum rules from non-relativistic quantum mechanics, five upper limits on the Rosseland mean opacity are calculated. One of them was obtained earlier by F. J. Dyson.

In two reports from General Atomic (GAMD-469 and GA-848), F. J. Dyson derives a maximum value for the Rosseland mean opacity. In this paper, some more upper limits to the opacity will be derived.

The Rosseland mean opacity, $\bar{K}$, is defined by

$$\frac{1}{\bar{K}} = \int_0^\infty \frac{w'(u)\, du}{K'(\nu)} ,$$

where

$$w'(u) = \frac{15}{4\pi^4} \frac{u^4 e^u}{\left(1-e^u\right)^2} , \quad u = h\nu/kT,$$

and $K'(\nu)$ is the absorption coefficient corrected for induced emission. Schwarz's inequality gives

$$\int_0^\infty \frac{w'(u)\, du}{K'(\nu)} \cdot \int_0^\infty u^\ell\, K'(\nu)\, du \geq \left[\int_0^\infty \sqrt{w'(u)\, u^\ell}\, du\right]^2 .$$

The integral on the right side of the inequality is easily evaluated. For some values of ℓ, the second integral on the left can be evaluated by the use of sum rules. Dyson did this for $\ell = 0$. We will repeat his derivation in somewhat greater detail than in the General Atomic reports and also do the cases $\ell = 2$ and -2.

The absorption coefficient, $K'(\nu)$, is

$$\sum_{j>i} \left(N_i - N_j\right) \cdot \frac{1}{\rho} \cdot \sigma_{ij} (\nu),$$

where N_i and N_j are numbers of atoms per unit volume in states i and j, ρ is the mass density, and $\sigma_{ij}(\nu)$ is the cross-section of an atom in state i for absorption of a photon of frequency ν with the atom ending in state j. The sum is over all states of the atom with $E_j > E_i$ and over all initial states i.

In the non-relativistic electric dipole approximation

$$\sigma_{ij} (\nu) = \frac{2\pi e^2}{m^2 c \nu} \cdot \delta\left(E_j - E_i - h\nu\right) \cdot \left| \left(\sum_n \underline{\epsilon} \cdot \underline{p}_n\right)_{ij} \right|^2 .$$

This may be written using the well known dimensionless oscillator strengths

$$f_{ji} = \frac{2i}{\hbar} p_{ij} \, x_{ji} = \frac{m}{\hbar^2} \left(E_j - E_i\right) \left| x_{ji} \right|^2$$

$$= \frac{2}{m} \frac{\left|p_{ji}\right|^2}{E_j - E_i} = - f_{ij},$$

where

$$x = \sum_n \underline{\epsilon} \cdot \underline{r}_n, \; p = \sum_n \underline{\epsilon} \cdot \underline{p}_n .$$

The result is

$$\sigma_{ij} (\nu) = \frac{\pi e^2 h}{mc} \, \delta\left(E_j - E_i - \hbar\nu\right) f_{ji} .$$

The evaluation of $\int_0^\infty K'(\nu) \, du$ proceeds as follows:

$$\int_0^\infty K'(\nu) \, du = \frac{1}{kT} \sum_{j>i} \left(N_i - N_j\right) \cdot \frac{1}{\rho} \cdot \frac{\pi e^2 h}{mc} f_{ji} .$$

The terms being summed are symmetric under the interchange of i and j $\left(\left(N_i - N_j\right) f_{ji} = N_j - N_i\right) f_{ij}\Big)$, and the following is immediately obtained:

$$\int_0^\infty K'(\nu)\; du = \frac{1}{2kT} \cdot \frac{1}{\rho} \cdot \frac{\pi e^2 h}{mc} \cdot \sum_{ij} \left(N_i - N_j\right) f_{ji} .$$

The summation is now over all i and j; the i = j term can be included since it is zero. Using the sum rule

$$\sum_j f_{ji} = Z$$

(see the Appendix), we easily get

$$\sum_i N_i \sum_j f_{ji} = \sum_i N_i \cdot Z = NZ,$$

and

$$\sum_j N_j \sum_i \left(-f_{ji}\right) = \sum_j N_j \sum_i f_{ij} = NZ.$$

Thus

$$\int_0^\infty K'(\nu)\; du = 2\pi^2 \left(\frac{e^2/a_0}{kT}\right) \cdot \frac{NZ}{\rho} \cdot \frac{\hbar}{mc}\, a_0 \; .$$

The case $\ell = 2$ is handled similarly:

$$\int_0^\infty u^2 K'\;(\nu)\, du = \frac{1}{(kT)^3} \sum_{j>i} \left(N_i - N_j\right) \cdot \frac{1}{\rho} \cdot \frac{\pi e^2 h}{mc} \left(E_j - E_i\right)^2 f_{ji} .$$

The summation may again be extended to all j and i by the use of the symmetry under interchange of j and i:

$$\int_0^\infty u^2 K'(\nu)\; du = \frac{1}{2(kT)^3} \cdot \frac{1}{\rho} \cdot \frac{\pi e^2 h}{mc} \sum_{ij} \left(N_i - N_j\right) \left(E_j - E_i\right)^2 f_{ji} .$$

The sum rule

$$\sum_j \left(E_j - E_i\right)^2 f_{ji} = \frac{4\pi Z e^2 \hbar^2}{3m} \left(\sum_{mn} \delta\left(\underline{r}_n - \underline{R}_m\right)\right)_{ii}$$

is used where, as explained in the Appendix, an average over propagation directions and polarizations has been performed. The sums

$$\sum_i N_i \sum_j \left(E_j-E_i\right)^2 f_{ji} = \sum_i N_i \frac{4\pi Z e^2\hbar^2}{3m} \left(\sum \delta\left(\underline{r}_n-\underline{R}_m\right)\right)_{ii}$$

and

$$\sum_j N_j \sum_i - \left(E_j-E_i\right)^2 f_{ji} = \sum_j N_j \frac{4\pi Z e^2\hbar^2}{3m} \left(\sum \delta\left(\underline{r}_n-\underline{R}_m\right)\right)_{ii}$$

are done, and there results

$$\int_0^\infty u^2 K'(\nu)\, du \approx 2\pi^2\left(\frac{e^2}{a_0 kT}\right)^3 \cdot \frac{\hbar}{mc} a_0 \cdot \sum_i \frac{N_i Z}{\rho} \left(\frac{4\pi}{3} a_0^3 \sum \delta\left(\underline{r}_n-\underline{R}_m\right)\right)_{ii}.$$

When $\ell = -2$,

$$\int_0^\infty u^{-2} K'(\nu)\, du = kT \cdot \sum_{j>i} \left(N_i-N_j\right) \cdot \frac{1}{\rho} \cdot \frac{\pi e^2 h}{mc} \left(E_j-E_i\right)^{-2} f_{ji}.$$

By the use of symmetry the sum may be extended to all states for which $E_j \neq E_i$:

$$\int_0^\infty u^2 K'(\nu)\, du = \frac{1}{2} kT \cdot \sum_{j,i}{}' \left(N_i-N_j\right) \cdot \frac{1}{\rho} \cdot \frac{\pi e^2 h}{mc} \left(E_j-E_i\right)^{-2} f_{ji}.$$

The sum rule

$$\sum_j{}' \left(E_j-E_i\right)^{-2} f_{ji} = \frac{2m}{\hbar^2 e^2} \alpha_i'$$

is now used with the result that

$$\int_0^\infty u^{-2} K'(\nu)\, du = 2\pi^2\left(\frac{a_0 kT}{e^2}\right) \cdot \frac{\hbar}{mc} a_0 \cdot \sum_i 2 \frac{N_i}{\rho} \left(\alpha_i / a_0^3\right).$$

It should be noted in the preceding that the use of Schwarz's inequality requires that $K'(\nu) \geq 0$. This will be true only if $N_i \geq N_j$ when $E_i \leq E_j$. This means that the state of the matter must be such that the lower energy states are more highly occupied than higher energy states. Otherwise there is no restriction on the state of the matter.

Ordinarily the Rosseland opacity is used when the matter is in local thermodynamic equilibrium with the radiation. If this is the case, then

$$N_j = N_i \, e^{-h\nu/kT} ,$$

and

$$K'(\nu) = \sum_{if} N_i \left(1-e^{-u}\right) \cdot \frac{1}{\rho} \cdot \sigma_{if}(\nu)$$

$$= e^{-u}\left(e^{u}-1\right) K(\nu) .$$

The last equation defines $K(\nu)$. The Rosseland mean opacity may then be written

$$\frac{1}{\bar{K}} = \int_0^\infty \frac{w(u)\,d\,u}{K(\nu)} ,$$

where

$$w(u) = \frac{15}{4\pi^4} \, \frac{u^4 e^{2u}}{\left(e^{u}-1\right)^3} .$$

The Schwarz inequality gives

$$\int_0^\infty \frac{w(u)du}{K(u)} \cdot \int_0^\infty u^{\ell} K(\nu)\, du \geq \left[\int_0^\infty \sqrt{w(u)\; u^{\ell}}\, d\,u\right]^2 .$$

The second integral on the left cannot be evaluated exactly by sum rules as before, but an upper limit can be found for it.

First consider the case, $\ell = 1$. Then

$$\int_0^\infty uK(u)\, du = \frac{1}{(kT)^2} \sum_{j>i} N_i \cdot \frac{1}{\rho} \cdot \frac{\pi e^2 h}{mc} \left(E_j - E_i\right) f_{ji} .$$

The sum can now be extended to states with $E_j \leq E_i$ and an inequality obtained:

$$\int_0^\infty uK(u)\,du \le \frac{1}{(kT)^2}\cdot\frac{1}{\rho}\cdot\frac{\pi e^2 h}{mc}\sum_{i,j} N_i\left(E_j-E_i\right) f_{ji}\,.$$

The right side of the inequality may be substituted for the integral in the Schwarz inequality, and the inequality will be preserved.

The sum rule

$$\sum_j \left(E_j-E_i\right) f_{ji} = \frac{4}{3}\left(\sum_n \frac{\underline{p}_n^{\,2}}{2m} + \sum_{n,n'}{}' \frac{\underline{p}_n\cdot\underline{p}_{n'}}{2m}\right)_{ii}$$

is now used, and one obtains

$$\int_0^\infty uK(u)\,du \le 2\pi^2\left(\frac{e^2/a_0}{kT}\right)^2\cdot\frac{\hbar}{mc}\,a_0\cdot\sum_i\frac{N_i}{\rho}\cdot\frac{4}{3}\left(\sum_n\frac{\underline{p}_n^{\,2}}{2m}+\sum_{nn'}\frac{\underline{p}_n\cdot\underline{p}_{n'}}{2m}\right)_{ii}\frac{1}{e^2/a_0}.$$

When $\ell = -1$ the integral to be considered is

$$\int_0^\infty \frac{1}{u}\,K(u)\,du = \sum_{j>i} N_i\cdot\frac{1}{\rho}\cdot\frac{\pi e^2 h}{mc}\,\frac{1}{E_j-E_i}\,f_{ji}$$

which is less than

$$\sum_{j,i}{}' N_i\cdot\frac{1}{\rho}\cdot\frac{\pi e^2 h}{mc}\,\frac{f_{ji}}{E_j-E_i}\,.$$

This time the sum rule

$$\sum_j{}'\frac{f_{ji}}{E_j-E_i} = \frac{2m}{3\hbar^2}\left(\sum_{nn'}\underline{r}_n\cdot\underline{r}_{n'}\right)_{ii}$$

is employed to give

$$\int_0^\infty\frac{1}{u}\,K(u)\,du\le 2\pi^2\cdot\frac{\hbar}{mc}\,a_0\sum_i\frac{N_i}{\rho}\cdot\frac{2}{3}\left(\sum_{nn'}\underline{r}_n\cdot\underline{r}_{n'}\right)_{ii}\frac{1}{a_0^{\,2}}.$$

The five limits on the Rosseland mean opacity can be summarized. Writing $\overline{K} \le \overline{K}_\ell$, we have

$$\overline{K}_2 = \frac{1}{S_2{}^2} \cdot 2\pi^2 \left(\frac{e^2}{\hbar c}\right)\left(\frac{e^2}{a_0 kT}\right)^3 a_0{}^2 \sum_i \frac{N_i Z}{\rho} \frac{4\pi}{3} a_0{}^3 \left(\sum_{mn} \delta\left(\underline{r}_n - \underline{R}_m\right)\right)_{ii},$$

$$\overline{K}_1 = \frac{1}{S_1{}^2} \cdot 2\pi^2 \left(\frac{e^2}{\hbar c}\right)\left(\frac{e^2}{a_0 kT}\right)^2 a_0{}^2 \sum_i \frac{N_i}{\rho} \cdot \frac{4}{3} \left(\sum_{nn'} \frac{\underline{p}_n \cdot \underline{p}_{n'}}{2m}\right)_{ii} \frac{1}{e^2/a_0}.$$

$$\overline{K}_0 = \frac{1}{S_0{}^2} \cdot 2\pi^2 \left(\frac{e^2}{\hbar c}\right)\left(\frac{e^2}{a_0 kT}\right) a_0{}^2 \frac{NZ}{\rho},$$

$$\overline{K}_{-1} = \frac{1}{S_{-1}{}^2} \cdot 2\pi^2 \left(\frac{e^2}{\hbar c}\right) a_0{}^2 \sum_i \frac{N_i}{\rho} \cdot \frac{2}{3} \left(\sum_{nn'} \underline{r}_n \cdot \underline{r}_{n'}\right)_{ii} \frac{1}{a_0{}^2},$$

$$\overline{K}_{-2} = \frac{1}{S_{-2}{}^2} \cdot 2\pi^2 \left(\frac{e^2}{\hbar c}\right)\left(\frac{a_0 kT}{e^2}\right) a_0{}^2 \sum_i 2 \frac{N_i}{\rho} \left(\alpha_i / a_0{}^3\right).$$

The constants S_ℓ are

$$S_2 = \frac{\sqrt{15}}{2\pi^2} \int_0^\infty u^3 \, e^{-u/2} \frac{du}{1-e^{-u}} = 19.112,$$

$$S_1 = \frac{\sqrt{15}}{2\pi^2} \int_0^\infty u^{5/2} \, e^{-u/2} \frac{du}{(1-e^{-u})^{3/2}} = 7.704,$$

$$S_0 = \frac{\sqrt{15}}{2\pi^2} \int_0^\infty u^2 \, e^{-u/2} \frac{du}{1-e^{-u}} = 3.302,$$

$$S_{-1} = \frac{\sqrt{15}}{2\pi^2} \int_0^\infty u^{3/2} \, e^{-u/2} \frac{du}{\left(1-e^{-u}\right)^{3/2}} = 1.741,$$

$$S_{-2} = \frac{\sqrt{15}}{2\pi^2} \int_0^\infty u \, e^{-u/2} \frac{du}{1-e^{-u}} = 0.9682.$$

An example in which $\overline{K}_2$ gives a much better limit on the opacity than $\overline{K}_0$ is shown in the table. The values for K are taken from GA - 848 and omit the contribution from lines. The correct values should be somewhat larger.

It should be noted that care must be used in calculating matrix elements such as $\left(\delta(\underline{r}) \right)_{ii}$. For unbound states the results from the correct Coulomb wave functions may be rather different from those using plane waves.

Opacity of Hydrogen

ρ g/cm^3	kT ev	K cm^2/g	$\overline{K}_2$ cm^2/g	$\overline{K}_0$ cm^2/g
3.64x10^{-3}	5	9.71x10^{4}	54.6 x10^{4}	1.2x10^{6}
6.52x10^{-4}	5	3.39x10^{4}	19.0 x10^{4}	1.2x10^{6}
2.40x10^{-4}	5	1.47x10^{4}	8.21x10^{4}	1.2x10^{6}
5.74x10^{-5}	5	3.85x10^{3}	21.4 x10^{3}	1.2x10^{6}
2.28x10^{-5}	5	1.55x10^{3}	8.66x10^{3}	1.2x10^{6}
5.67x10^{-6}	5	3.90x10^{2}	21.7 x10^{2}	1.2x10^{6}
7.40x10^{-3}	10	8.09x10^{3}	26.5 x10^{3}	6.2x10^{5}
1.66x10^{-3}	10	2.25x10^{3}	7.3 x10^{3}	6.2x10^{5}
6.50x10^{-4}	10	9.21x10^{2}	29.8 x10^{2}	6.2x10^{5}
1.61x10^{-4}	10	2.33x10^{2}	7.5 x10^{2}	6.2x10^{5}
6.41x10^{-5}	10	9.34x10^{1}	30.1 x10^{1}	6.2x10^{5}
1.60x10^{-5}	10	2.34x10^{1}	7.5 x10^{1}	6.2x10^{5}
1.95x10^{-2}	20	704	2270	3x10^{5}
4.62x10^{-3}	20	186	591	3x10^{5}
1.83x10^{-3}	20	75.4	239	3x10^{5}
4.54x10^{-3}	20	19.0	60	3x10^{5}
1.81x10^{-4}	20	7.59	24	3x10^{5}
4.53x10^{-5}	20	1.90	6.0	3x10^{5}

APPENDIX

The Sum Rules.

The evaluation of sums of the form

$$S_\ell = \sum_b f_{ba} \left(E_b - E_a\right)^\ell$$

where the f_{ba} are the dimensionless oscillator strengths:

$$f_{ba} = + \frac{2i}{\hbar} p_{ab} x_{ba} = - \frac{2i}{\hbar} x_{ab} p_{ba}$$

may be found in the literature. For the sake of completeness they are included here.

The sums S_ℓ diverge for $\ell < -2$ and $\ell > +2$, and it is only for the integral values 0, ±1, and ±2 that the sums can be evaluated by algebraical methods.

First, the definitions of p and x should be put down

$$p = \sum_n \underline{\epsilon} \cdot \underline{p}_n \ , \ x = \sum_n \underline{\epsilon} \cdot \underline{r}_n ,$$

where $\underline{\epsilon}$ is a unit polarization vector which may be in the direction of the x axis. Also we write

$$\frac{\partial}{\partial x} = \sum_n \underline{\epsilon} \cdot \underline{\nabla}_n \ .$$

The positions of the nuclei of the atoms are $\underline{R}_m$ and are regarded as fixed. We can assume that $\sum_m \underline{R}_m = 0$.

Next, the equations for the rate of change of p and x are

$$\frac{dx}{dt} = \frac{i}{\hbar}\left(Hx-xH\right) = \frac{p}{m} \text{ and } \frac{dp}{dt} = \frac{i}{\hbar}\left(Hp-pH\right) = -\frac{\partial V}{\partial x}.$$

These will also be used. Let us take up the five cases in order.

$\ell = -2$.

The equation for $\frac{dx}{dt}$ gives this relation between p_{ab} and x_{ab}:

$$\frac{1}{m} p_{ab} = \frac{i}{\hbar}\left(E_a - E_b\right) x_{ab}\ .$$

Using this

$$S_{-2} = \frac{2m}{\hbar^2} \sum_b \frac{x_{ab}x_{ba}}{E_b - E_a}$$

$$= \frac{2m}{\hbar^2 e^2}\,\alpha'.$$

The sum excludes states for which $E_b = E_a$. α' is the polarizability of an atom which can be measured or, in principle at least, evaluated by variational methods. The sum itself cannot be further reduced.

$\ell = -1$.

From the matrix relation used in the $\ell = -2$ case it is easily seen that

$$S_{-1} = \frac{2m}{\hbar^2} \sum_b x_{ab}x_{ba}.$$

The terms where $E_a = E_b$ give $x_{ab} = 0$ except for accidental degeneracies like those in the hydrogen atom. Including all states b, the completeness relation gives

$$S_{-1} = \frac{2m}{\hbar^2}\left(x \cdot x\right)_{aa}$$

$$= \frac{2m}{\hbar^2}\left(\sum_{nn'} \underline{\epsilon}\cdot\underline{r}_n\ \underline{\epsilon}\cdot\underline{r}_{n'}\right)_{aa} .$$

On averaging over polarization vectors $\underline{\epsilon}$ or over states a which differ from each other only in the magnetic quantum number, one obtains

$$\widetilde{S}_{-1} = \frac{2m}{3\hbar^2}\left(\sum_{nn'} \underline{r}_n\cdot\underline{r}_{n'}\right)_{aa} .$$

This form of the sum rule is used in the opacity limits.

$\ell = 0.$

This is the well known Thomas - Reiche - Kuhn sum rule, and is particularly simple. One uses the definition of the oscillator strengths and the commutation relations:

$$S_0 = \sum_b f_{ba} = \frac{1}{2}\sum_b \frac{2i}{\hbar}\left(p_{ab}x_{ba} - x_{ab}p_{ba}\right)$$

$$= \frac{i}{\hbar}\left(px - xp\right)_{aa} = \left(\frac{\partial}{\partial x}\, x\right)_{aa}$$

$$= \left(\sum_{nn'} \delta_{nn'}\right)_{aa} = Z .$$

Since $p_{ab} = \frac{im}{\hbar}\left(E_a - E_b\right)x_{ab}$ vanishes for $E_a = E_b$, these terms may be included or dropped as one pleases. This is the case also for $\ell = 1$ and 2.

$\ell = 1.$

We have

$$S_1 = \sum_b \frac{2i}{\hbar}\, p_{ab}\left(E_b - E_a\right)x_{ba}$$

$$= \frac{2i}{\hbar}\left(pHx - pxH\right)_{aa}$$

using completeness. But the equation for $\frac{dx}{dt}$ gives us

$$S_1 = \frac{2}{m}\left(pp\right)_{aa}$$

$$= \frac{2}{m}\left(\sum_{nn'} \underline{\epsilon}\cdot\underline{p}_n \; \underline{\epsilon}\cdot\underline{p}_{n'}\right)_{aa}.$$

The same average that was performed in the case of $\ell = -1$ gives

$$\widetilde{S}_1 = \frac{2}{3m}\left(\sum_{nn'} \underline{p}_n \cdot \underline{p}_{n'}\right)_{aa}.$$

Returning to the first equation in this section, we can write

$$S_1 = \sum_b \frac{2i}{\hbar}\, p_{ab}\left(E_b - E_a\right) x_{ba}$$

$$= \frac{2i}{\hbar}\left(pHx - Hpx\right)_{aa}.$$

Now, using the equation for $\frac{dp}{dt}$, one has

$$S_1 = 2\left(\frac{\partial V}{\partial x}\, x\right)_{aa}$$

$$= 2\left(\sum_{nn'} \underline{\epsilon}\cdot\underline{r}_n \; \underline{\epsilon}\cdot\underline{\nabla}_{n'}\, V\right)_{aa}.$$

The potential for a many atom system is

$$V = Ze^2 \sum_{m,k} \frac{1}{\left|\underline{r}_k - \underline{R}_m\right|} + \frac{1}{2}\, e^2 \sum_{k,\ell}{}' \frac{1}{\underline{r}_{k\ell}}.$$

The inter-electron terms in V vanish when all the derivatives are taken.

There remains

$$S_1 = -2Ze^2\left(\sum_{mnn'} \underline{\epsilon}\cdot\underline{r}_{n'} \; \underline{\epsilon}\cdot\underline{\nabla}_n \frac{1}{\left|\underline{r}_n - \underline{R}_n\right|}\right)_{aa}$$

$$= 2Ze^2\left(\sum_{mnn'} \underline{\epsilon}\cdot\underline{r}_{n'} \; \underline{\epsilon}\cdot\left(\underline{r}_n - \underline{R}_m\right) \Big/ \left|\underline{r}_n - \underline{R}_{m'}\right|^3\right)_{aa}.$$

The average value of S_1 is

$$\widetilde{S}_1 = \frac{2Ze^2}{3}\left(\sum_{mnn'} \underline{r}_{n'} \cdot \left(\underline{r}_n - \underline{R}_m\right) \Big/ \left|\underline{r}_n - \underline{R}_m\right|^3\right)_{aa}.$$

The two values for S_1 and for $\widetilde{S}_1$ must, of course, be equal although their forms are rather different.

$\underline{\ell = 2.}$

This case is a little more complicated.

We have

$$S_2 = \sum_b \frac{2i}{\hbar} p_{ab} \left(E_b - E_a\right)^2 x_{ba}$$

$$= \frac{2i}{\hbar} \left(pH^2x - 2pHxH + pxH^2\right)_{aa}$$

$$= \frac{2}{m} \left(pHp - ppH\right)_{aa}$$

$$= \frac{2i\hbar}{m}\left(p \frac{\partial V}{\partial x}\right)_{aa},$$

and also

$$S_2 = -\sum_b \frac{2i}{\hbar} x_{ab} \left(E_b - E_a\right)^2 p_{ba}$$

$$= -\frac{2i}{\hbar} \left(xH^2p - 2HxHp + H^2xp\right)_{aa}$$

$$= -\frac{2}{m} \left(Hpp - pHp\right)_{aa}$$

$$= -\frac{2i\hbar}{m}\left(\frac{\partial V}{\partial x} p\right)_{aa}.$$

Combining the last expressions for S_2 gives

$$S_2 = \frac{i\hbar}{m}\left(p \frac{\partial V}{\partial x} - \frac{\partial V}{\partial x} p\right)_{aa}$$

$$= \frac{\hbar^2}{m}\left(\frac{\partial}{\partial x}\;\frac{\partial V}{\partial x}\right)_{aa}.$$

The definitions of $\frac{\partial}{\partial x}$ and V are now used to further reduce the expression for S_2:

$$S_2 = \frac{\hbar^2}{m}\left(\sum_{nn'}\;\underline{\epsilon}\cdot\underline{\nabla}_n\;\underline{\epsilon}\cdot\underline{\nabla}_{n'}\;V\right)_{aa}$$

$$= -\,\frac{Ze^2\hbar^2}{m}\left(\sum_{mn}\;\underline{\epsilon}\cdot\underline{\nabla}_n\;\underline{\epsilon}\cdot\underline{\nabla}_n\;\frac{1}{|\underline{r}_n-\underline{R}_m|}\right)_{aa}.$$

When the average over $\underline{\epsilon}$ is taken, there results

$$\widetilde{S}_2 = \frac{4\pi}{3}\,\frac{Ze^2\hbar^2}{m}\left(\sum_{mn}\;\delta\left(\underline{r}_n-\underline{R}_m\right)\right)_{aa}.$$