where

$$B(r) = \beta_1 \exp\left[-\frac{r-a_0}{\rho}\right] - \beta_2 \left(\frac{a_0}{r}\right)^6,$$

and Ω_{12} specifies the direction of $\boldsymbol{r}_{12}$ relative to the c-axis. The theoretical values of the parameters are $\beta_1 = 2.6\,\mathrm{K}, \beta_2 = 1.6\,\mathrm{K}$, and $\rho = 0.283\,\text{Å}$; $a_0 = 3.75\,\text{Å}$ is the nearest neighbor distance in solid H_2 at $P = 0$. For computational simplicity, we retain only the $m = 0$ part of this interaction and have, upon comparison with eq. (10),

$$V^{20}(1,2) = V^{02}(1,2) = (\tfrac{8}{5}\sqrt{5})\pi\, B(r)\, P_2(\cos\theta_{12}), \quad (11)$$

where θ_{12} is the angle between $\boldsymbol{r}_{12}$ and the c-axis; P_2 is the Legendre polynomial of degree two. There is also an anisotropic potential proportional to $Y_2(\omega_1)\, Y_2(\omega_2)$. The dominant part of this is the electric quadrupole–quadrupole (EQQ) interaction which gives

$$V^{22}(1,2) = 20\pi\, \Gamma_0\, P_4(\cos\theta_{12}) \left(\frac{a_0}{r}\right)^5, \quad (12)$$

where $\Gamma_0 = 1$ K. Once again, we neglect terms with $m \neq 0$. Finally, there should also be terms in eq. (10) proportional to $Y_{2l}(\omega_1)$ and $Y_{2l}(\omega_2)$; the sum of all neglected terms is less than about 10% of V^{20} or V^{02} for all molar volumes treated here. In order to be consistent in this regard, we systematically ignore all terms involving $Y_4(\omega_1)$ and $Y_4(\omega_2)$ in what follows.

It is interesting to compare the exponential (valence) part of V_{ani} in eq. (11) with the corresponding part of the empirically determined E6 potential. The empirical constant $\rho_e = r_m/\alpha = 0.239$ Å is sufficiently different from the theoretical $\rho_t = 0.283$ Å to produce considerably different results in the calculations presented below if ρ_t is replaced by ρ_e. We shall comment further on this point in section 4.

3. Anisotropic formalism

The introduction of V_{ani} depending on the rotational state of the molecules produces an admixture of rotational states in the single-particle and correlation functions. When V_{ani} is taken in the form of eq. (10), then $\varphi_i(1)$ becomes

$$\varphi_i(1;\omega_1) = Y_0(\omega_1)\, \varphi_{0i}(1) + Y_2(\omega_1)\, \varphi_{2i}(1), \quad (13)$$

so that we now have two functions φ_{0i} and φ_{2i} to determine. Rotational states with $l > 2$ are ignored; this procedure is valid as long as the "anisotropy energy" is small compared to the excitation energy of these states.

Similarly, the single-particle self-consistent field now takes the form

$$u_i(1,\omega_1) = Y_0(\omega_1)\, Y_0(\omega_1)\, u_{0i}(1) + Y_0(\omega_1)\, Y_2(\omega_1)\, u_{2i}(1). \quad (14)$$

The Schrödinger equation for the single-particle function can be written as two equations:

$$\left(-\frac{\nabla_1^2}{2m} + u_{0i}\, Y_0^2\right)\varphi_{0i} + \tfrac{8}{7} u_{2i}\, Y_0^2\, \varphi_{2i} = \varepsilon\, \varphi_{0i}, \quad (15a)$$

$$\left(-\frac{\nabla_1^2}{2m} + 6B_I + u_{0i}\, Y_0^2 + (\tfrac{4}{21}\sqrt{5})\, u_{2i}\, Y_0^2\right)\varphi_{2i} + u_{2i}\, Y_0^2\, \varphi_{0i} = \varepsilon\, \varphi_{2i}, \quad (15b)$$

where we have used

$$Y_2\, Y_2 = (\tfrac{18}{35}\sqrt{\tfrac{5}{9}})\, Y_4\, Y_0 + (\tfrac{4}{21}\sqrt{5})\, Y_2\, Y_0 + \tfrac{8}{7}\, Y_0\, Y_0,$$

and Y_4 has been neglected, which is consistent with our approach of considering only the $l = 0, 2$ rotational states.

The general form of the correlation function $\chi_{ij}(1,2;\omega_1,\omega_2)$ is

$$\begin{aligned}\chi_{ij}(1,2;\omega_1,\omega_2) = 4\pi\, [&\chi_{ij}^{00}(1,2)\, Y_0(\omega_1)\, Y_0(\omega_2) \\ &+ \chi_{ij}^{20}(1,2)\, Y_2(\omega_1)\, Y_0(\omega_2) \\ &+ \chi_{ij}^{02}(1,2)\, Y_0(\omega_1)\, Y_2(\omega_2) \\ &+ \chi_{ij}^{22}(1,2)\, Y_2(\omega_1)\, Y_2(\omega_2)]\end{aligned} \quad (16)$$

in our approximation. We remark that χ_{ij} is part of the two-particle Green's function which has been factored into single-particle and correlation functions. This separation is not unique, and the form of χ_{ij} in eq. (16) is a consequence of our previous treatment (EBNER and SUNG, 1971b).

The self-consistent field is given by the same equation as before

$$u_i(1,\omega_1) = \sum_j{}' \int V(1,2)\, \chi_{ij}(1,2;\omega_1,\omega_2)\, |\varphi_j(2,\omega_2)|^2\, \mathrm{d}^3 r_2\, \mathrm{d}\omega_2\,. \quad (17)$$

The equation of motion for χ_{ij} is similar to eq. (4),

$$H_{ij}\, \chi_{ij}\, \varphi_i\, \varphi_j = \lambda_0\, \chi_{ij}\, \varphi_i\, \varphi_j, \quad (18)$$

where

$$H_{ij} = -\frac{\nabla_1^2}{2m} - \frac{\nabla_2^2}{2m} + \frac{1}{2I}J_1^2 + \frac{1}{2I}J_2^2 + V(1,2;\omega_1,\omega_2) + u_i(1,\omega_1) + u_j(2,\omega_2) + \Delta_{ij}(1,2) - \int \chi_{ij}(1,\bar{2};\omega_1,\bar{\omega}_2)\, V(1,\bar{2})\, |\varphi_j(\bar{2},\bar{\omega}_2)|^2\, \mathrm{d}^3\bar{r}_2\, \mathrm{d}\bar{\omega}_2 - \int \chi_{ij}(\bar{1},2;\bar{\omega}_1,\omega_2)\, V(\bar{1},2)\, |\varphi_i(\bar{1},\bar{\omega}_1)|^2\, \mathrm{d}^3\bar{r}_1\, \mathrm{d}\bar{\omega}_1, \tag{19}$$

where J_1^2 and J_2^2 are the internal angular momentum operators for molecules 1 and 2. The simultaneous solution of these equations plus the single-particle equation and the self-consistency condition eq. (17) is a formidable numerical problem. Since our interest at this time is primarily to examine the effect of the anisotropic interaction on the energy in the molecular phase rather than to pursue the question of a transition to the metallic phase, an expansion procedure will be used. We keep terms in V_{ani} through second order only. This means that we should find φ_{2i} and u_{2i} to first order in V_{ani} and φ_{0i} and u_{0i} to second order. If φ_{0i} is normalized to 1, then each single-particle wave function should be multiplied by $N_1^{-\frac{1}{2}}$, where

$$N_1 = \int \varphi_{0i}^2(1)\, \mathrm{d}^3\bar{r}_1 + \int \varphi_{2i}^2(1)\, \mathrm{d}^3 r_1 = 1 + \int \varphi_{2i}^2(1)\, \mathrm{d}^3 r_1 . \tag{20}$$

Also, to maintain the proper normalization of the two-particle Green's function, the correlation function should be divided by N_2, where

$$N_2 = 1 + 2\int [\chi_{ij}^{02}(1,2)\, \varphi_{0i}^2(1)\, \varphi_{0j}(2)\, \varphi_{2j}(2) + \chi_{ij}^{20}(1,2)\, \varphi_{0j}^2(2)\, \varphi_{0i}(1)\, \varphi_{2i}(1) + \chi_{ij}^{00}(1,2)\, \varphi_{0i}^2(1)\, \varphi_{2j}^2(2)]\, \mathrm{d}^3 r_1\, \mathrm{d}^3 r_2, \tag{21}$$

where we have used

$$\int \chi_{ij}^{00}(1,2)\, \varphi_{0i}^2(1)\, \varphi_{0j}^2(2)\, \mathrm{d}^3 r_1\, \mathrm{d}^3 r_2 = 1 .$$

The single-particle potential is given to the appropriate order in V_{ani} by

$$u_{0i}(1) = \sum_j{}' \int V^{00}\, \chi_{ij}^{00}\, \varphi_{0j}^2\, N_2^{-1}\, \mathrm{d}^3 r_2 + 2\sum_j{}' \int V^{00}\, \chi_{ij}^{02}\, \varphi_{0j}\, \varphi_{2j}\, \mathrm{d}^3 r_2 + 2\sum_j{}' \int V^{02}\, \chi_{ij}^{00}\, \varphi_{0j}\, \varphi_{2j}\, \mathrm{d}^3 r_2 + \sum_j{}' \int V^{00}\, \chi_{ij}^{00}\, \varphi_{2j}^2\, \mathrm{d}^3 r_2 + \sum_j{}' \int V^{02}\, \chi_{ij}^{02}\, \varphi_{0j}^2\, \mathrm{d}^3 r_2 + \tfrac{7}{8}\sum_j{}' \int V^{20}\, \chi_{ij}^{20}\, \varphi_{0j}^2\, \mathrm{d}^3 r_2 + \tfrac{7}{8}\sum_j{}' \int V^{22}\, \chi_{ij}^{22}\, \varphi_{0j}^2\, \mathrm{d}^3 r_2 \tag{22}$$

and

$$u_{2i}(1) = \sum_j{}' \int V^{20}\, \chi_{ij}^{00}\, \varphi_{0j}^2\, \mathrm{d}^3 r_2 + \sum_j{}' \int V^{00}\, \chi_{ij}^{20}\, \varphi_{0j}^2\, \mathrm{d}^3 r_2 . \tag{23}$$

The expression for u_{0i} is correct to second order in V_{ani} while u_{2i} is first order. In these equations, corrections to first order in V_{ani} only are needed in $\chi_{ij}^{II'}$. These are determined as follows: Eq. (18) is multiplied by $Y_0(\omega_1)\, Y_0(\omega_2)$ and integrated over ω_1 and ω_2 to give

$$H_{ij}^{00}\, \chi_{ij}^{00}\, \varphi_{0i}\, \varphi_{0j} = \lambda_0\, \chi_{ij}^{00}\, \varphi_{0i}\, \varphi_{0j},$$

where H_{ij}^{00} is the operator $\{\ldots\}$ in eq. (4). Thus χ_{ij}^{00} is just the correlation function of EBNER and SUNG (1971a). Of course, φ_{0i} differs from the single-particle function when V_{ani} is not present, but the difference is second-order and we shall ignore it. By also multiplying $Y_2(\omega_1)\, Y_0(\omega_2)$, $Y_0(\omega_1)\, Y_2(\omega_2)$ and $Y_2(\omega_1)\, Y_2(\omega_2)$ into eq. (18) and integrating over ω_1 and ω_2, we obtain three equations for the anisotropic part of the correlation function,

$$H_{ij}^{00}\, \chi_{ij}^{20}\, \varphi_{0i}\, \varphi_{0j} + 6B_I\, \chi_{ij}^{20}\, \varphi_{0i}\, \varphi_{0j} + 6B_I\, \chi_{ij}^{00}\, \varphi_{2i}\, \varphi_{0j} + H^{20}\, \chi_{ij}^{00}\, \varphi_{0i}\, \varphi_{0j} = \lambda_0\, \chi_{ij}^{20}\, \varphi_{0i}\, \varphi_{0j}, \tag{24}$$

$$H_{ij}^{00}\, \chi_{ij}^{02}\, \varphi_{0i}\, \varphi_{0j} + 6B_I\, \chi_{ij}^{02}\, \varphi_{0i}\, \varphi_{0j} + 6B_I\, \chi_{ij}^{00}\, \varphi_{0i}\, \varphi_{2j} + H^{02}\, \chi_{ij}^{00}\, \varphi_{0i}\, \varphi_{0j} = \lambda_0\, \chi_{ij}^{02}\, \varphi_{0i}\, \varphi_{0j} \tag{25}$$

and

$$H_{ij}^{00}\, \chi_{ij}^{22}\, \varphi_{0i}\, \varphi_{0j} + 12B_I\, \chi_{ij}^{22}\, \varphi_{0i}\, \varphi_{0j} + H^{22}\, \chi_{ij}^{00}\, \varphi_{0i}\, \varphi_{0j} = \lambda_0\, \chi_{ij}^{22}\, \varphi_{0i}\, \varphi_{0j}, \tag{26}$$

where

$$H^{02} = H^{20} = \frac{V^{20}}{4\pi}, \quad H^{22} = \frac{V^{22}}{4\pi}.$$